Geology of Ore Deposits, Vol. 47, No. 3, 2005, pp. 223–237. Translated from Geologiya Rudnykh Mestorozhdenii, Vol. 47, No. 3, 2005, pp. 249–264.

Genesis of the Tigrinoe Tin Deposit (Russia)

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Received September 28, 2004

Abstract—The paper presents results obtained by the authors and their colleagues while studying the Tigrinoe tin deposit, situated in northern Prymorye, in the central part of the Sikhote Alin accretionary fold region. Three ore stages are identified in the Tigrinoe deposit, though the period of its formation was relatively short (about 5 Ma), which is characteristic of deposits genetically associated with the rhyolite (ongonite)–leucogranite (Li–F type) magmatic association. The mineralogical–geochemical features of the stages distinguished and their relations with the ore-generating magmatism are described. A model of the evolution of the ore–magmatic system of the deposit is proposed.

INTRODUCTION

The Tigrinoe deposit is situated in the northern Prymorye region, in the Arminsk ore district, occupying the central part of the Sikhote Alin accretionary fold area. Twenty-four deposits have been discovered there (over an area of 10000 km^2), including the unique Vostok-2 skarn–scheelite–sulfide deposit, and over 200 ore occurrences of various metals. Prospecting completed in 1994 showed that the Tigrinoe deposit was a proper object for open-pit; its ores contain 0.115% Sn, 0.042% WO_3, and elevated concentrations of trace components: Zn, Bi, In, Cd, Ag, Ta, Nb, and Sc, which, appreciably raising the value of ores, give grounds to refer it to the Sn–W rare metal geochemical type. According to the genetic classification (Radkevich, 1968, 1975; *Geology of Tin Deposits…*, 1986), the deposit belongs to the cassiterite–quartz type. However, its area displays different indicated types, including quartz–feldspar, greisen with subtypes of topaz, siderophyllite (zinnwaldite), and mica–fluorite greisens, as well as quartz subtypes, occurring as sulfide-enriched cassiterite-bearing veins and closely spaced veinlet systems (linear stockworks) superimposed on greisens. Large ore volumes with scattered veinlet–disseminated ore mineralization, low concentrations of the main components, and the assignment of mineralization to granite porphyry stocks gave grounds for several researchers (Ivakin *et al.*, 1985) to attribute the Tigrinoe deposit to the large-scale tin porphyry type.

GEOLOGY OF THE DEPOSIT

The Tigrinoe deposit is localized in the western part of the Arminsk ore district, in the central part of the Glavnaya (Radkevich, 1958; Ivanov, 1971) or Luzhkinsk (Khanchuk *et al.*, 1995) tin-bearing zone (Sikhote Alin). In the west, the ore district (Fig. 1) is bordered by the Central Sikhote Alin fault, and, in the east, by structures of the Eastern Sikhote Alin volcanic belt. The deposit is a part of the Tigrinoe ore field, which, along with the Tigrinoe deposit, includes several W and Sn ore occurrences (Granitnoe, Vernoe, and others; Fig. 1).

As reported by Rodionov *et al.* (1984), Ivakin *et al.* (1985), Nikogosyan (1988), and other researchers, the ore field area (about 1000 km^2) is located in the peripheral zone of an arched uplift of the same name. The area is dominated by rocks of the Zhuravlevsk terrane (Khanchuk *et al.*, 1995), intruded by the Izluchinsk granitoid massif. South of the W–E trending Tigrinsk fault, which crosses the uplift, an Early Cretaceous flyschoid sequence developed, to which the Tigrinoe deposit (Fig. 2) is assigned. The Tigrinoe deposit formed in the apical zone of the granitoid massif, at the crossing of regional tectonic fractures of north–northwestern (Central Sikhote Alin) and east–northeastern (Tigrinsk) trend.

The structural factors of the deposit localization and different stages of ore mineralization were chiefly dominated by regional faults of N–S (Central Sikhote Alin) and W–E (Tigrinsk) strike. Structures of almost latitudinal trending must have controlled the position and morphology of the Tigrinoe intrusive, its stocks and apophyses, and its early-stage Mo mineralization, while almost N–S structures may (additionally) have controlled the distribution of ore-bearing veins and veinlets of the later tin–tungsten stage, which were mostly formed in closely spaced fractures of a northwestern (315°–340°) trend.

We suppose that a steeply dipping and oval-shaped in plan zone of breccias that was formed at the crossing of nearly N–S and W–E trending fractures is genetically and structurally important. Most researchers suggest that its nature is hydrothermal–explosive. At the

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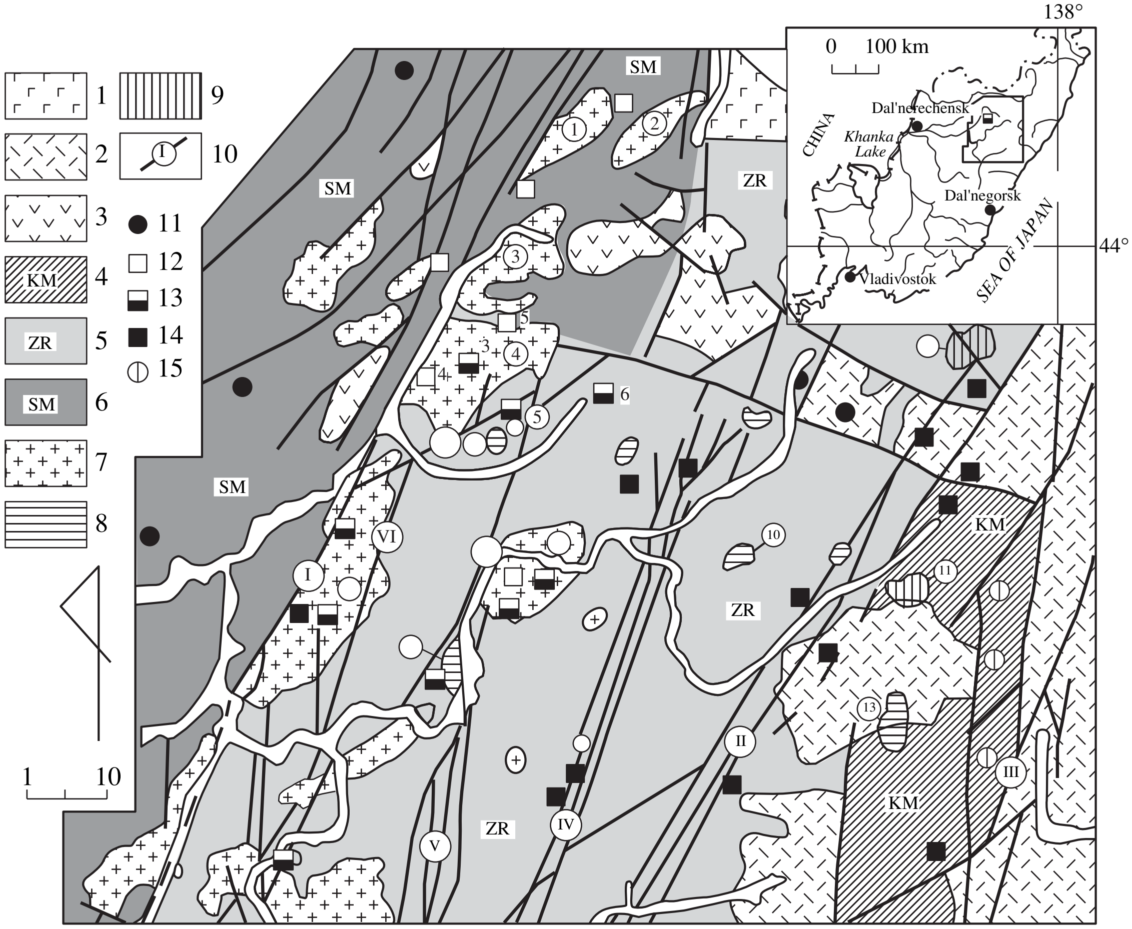

Fig. 1. Geological–metallogenic scheme of the Arminsk district modified after Utkin (1989). (1) Oligocene–Miocene basalts; (2, 3) effusives of the Eastern Sikhote Alin belt: (2) essentially andesites, (3) essentially rhyolites; (4) rock complexes of the Kemsk island arc terrane; (5) rock complexes of the Zhuravlevsk turbidite terrane; (6) rock complexes of the Samarkinsk accretionary prism; (7–9) intrusive associations: (7) granodiorite (adamellite)–granite, (8) gabbro–monzodiorite–granodiorite, (9) gabbro–monzonite–syenite; (10) fault zones: I, Central Sikhote Alin, II, Eastern, III, Kemsk, IV, Mikulinsk, V, Arminsk, VI, Berezovsk, VII, Parallelnaya, VIII, Tigrinsk; (11–15) deposits (ore occurrences): (11) gold, (12) tungsten, (13) tungsten–tin, (14) base metals–tin, (15) base metals (tin-free). Deposit of the Tigrinoe ore field: (1) Tigrinoe, (2) Vostok-2, (3) Vernoe, (4) Granitnoe, (5) Poputnoe, (6) Strannikovoe. Massifs: (1) Bisernyi, (2) Kayalu, (3) Dal'nensk, (4) Izluchinsk, (5) Tigrinsk, (6) Burelomnyi, (7) Dal'ne-Arminsk, (8) Arminsk, (9) Ust'-Mikulinsk, (10) Mechta, (11) Molodezhnyi, (12) Pravovalinkuisk, (13) Gornyi.

770-m level, it is situated close to the central part of the Malyi stock, which in this zone is also steeply dipping and complicated by N–S and W–E apophyses. Updip, the zone of breccias comes out of the Malyi stock and, above the 850-m level, is located in hornfels-altered host rocks (Fig. 3).

The central part of the ore field is occupied by the Bol'shoi stock, the composition of which is dominated by rhyolite and granite porphyries, and by the Malyi stock, composed of diversely greisenized leucocratic granites, which are outcrops of the Tigrinoe intrusive, concealed at a depth (geophysical data). The intrusive occurs parallel with a dike complex (apophyses) of subintrusive rhyolites. The peripheral zone comprises dikes of pre-granite ongorhyolites and monzonitoids (porphyrites), a stock of which (an intrusive of Burelomnyi Creek) is located at a distance of 4 km to the southwest from the deposit, and dikes of postore olivine basalts.

The Malyi stock has been most thoroughly studied (Gonevchuk, Gonevchuk, 1988, 1991; Korostelev *et al.*, 1990; Rodionov and Rodionova, 1980; Rodionov *et al.*, 1984; Rub *et al.*, 1986, 1991, 1998; Belyatsky *et al.*, 1998; Gonevchuk *et al.*, 1998; and others). The pipelike and, in plan, nearly oval-shaped body of the Malyi stock, dipping to the south at angles of 30°–50°, is complicated by sublatitudinal and submeridional (concordant with the ore-bearing structures) apophyses. The size of the stock (350 × 102 m) is maximum at the 850-m level, diminishing towards the top and bottom. Marginal pegmatite—stockscheider—is developed along the southern part of the level; its thickness amounts to 6 m, wedging out to the north. Hornfels fragments occurring in the stock endocontact are

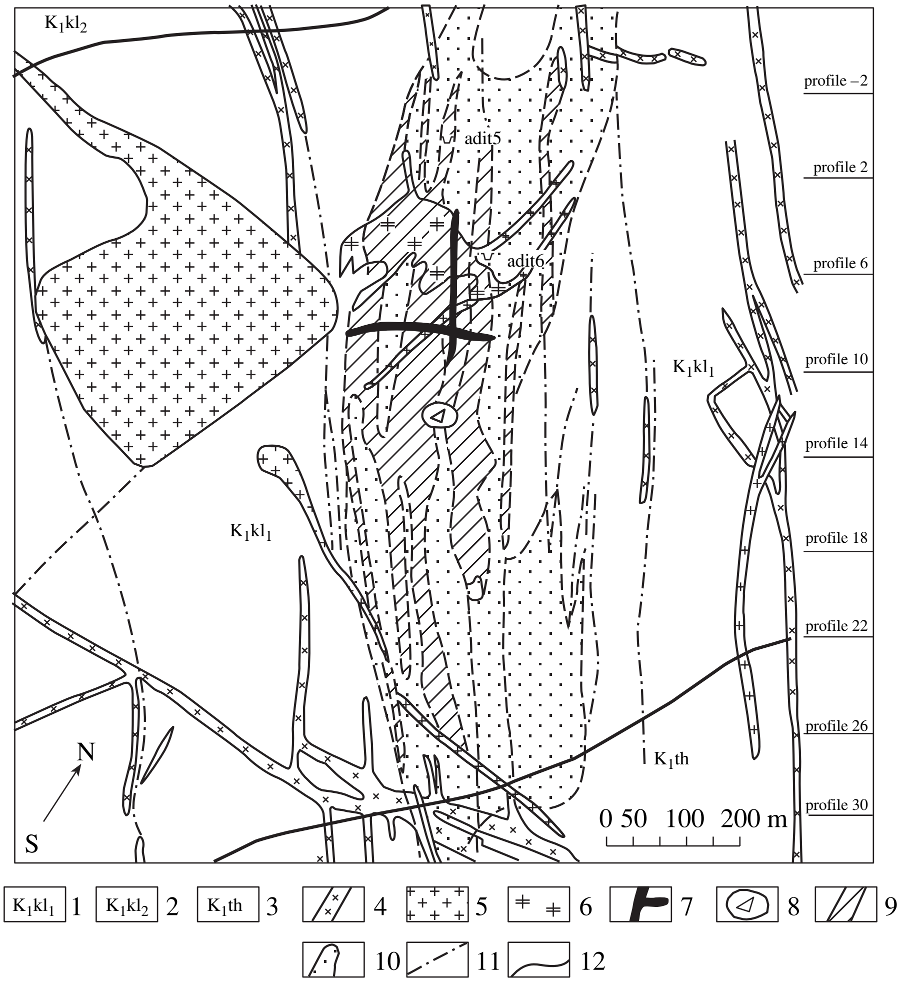

Fig. 2. Schematic geological map of the Tigrinoe deposit (based on data of I.A. Gaev, Yu.S. Sergeev, V.M. Akimov, and V.V. Orlovskii with supplements). (1) Upper bed of the Klyuchevsk suite: sandstones with siltstone interbeds; (2) lower bed of the Klyuchevsk suite: sandstones, siltstones, interlayers and lenses of gravelites and conglomerates; (3) Taukhinsk suite: laminated siltstones with interlayers of sandstones and claystones; (4) porphyry dikes (K_2^1); (5) granite–porphyries of the Bol'shoi stock (K_2^2); (6) porphyritic granites of the Malyi stock (K_2^3); (7) Paleogene basalts; (8) hydrothermal–explosive breccia; (9) veinlet–stockwork and greisen orebodies; (10) mineralized zones; (11) fractures; (12) geological boundaries.

rimmed by fine-grained albitites, thus demonstrating an active form of melt intrusion. Rhyolite dikes associated with granites were formed before the emplacement of the stock and are dissected by granite apophyses without appreciable displacement.

From the surface to a depth of about 200 m, the Malyi stock is composed of medium-grained (porphyritic) protolithionite and protolithionite–zinnwaldite granites, supposed to be facial varieties. Porphyritic granites are encountered in deeper zones (in porphyritic "pea-shaped" quartz segregations; the bulk mass is finely crystalline) with light rose zinnwaldite. Zones of pegmatoid granites and of strongly silicified rocks and quartzites (regarded by some researchers as liquation "silexites") are assigned to the contact between these varieties (Ruchkin *et al.*, 1987).

The Bol'shoi stock (Figs. 2, 3) is located some 120 m west of the Malyi stock. Hornfelses identified in the interval between them are intensely silicified closer to the contact with the Bol'shoi stock, while abundant siderophyllite and zinnwaldite inclusions are developed near the contact with the Malyi stock.

According to their structural–lithologic features, rocks of the Bol'shoi stock could be attributed to a subvolcanic variety of leucocratic granite–porphyries or porphyritic rhyolites. Granites of the stock acquire a clear subvolcanic appearance at the contact with terrigenous host rocks, where they may be accompanied by stockscheiders and explosive breccias.

Geological observations and geochemical evidence (including isotopic) suggest that the three described granite varieties developed in different phases. The ear-

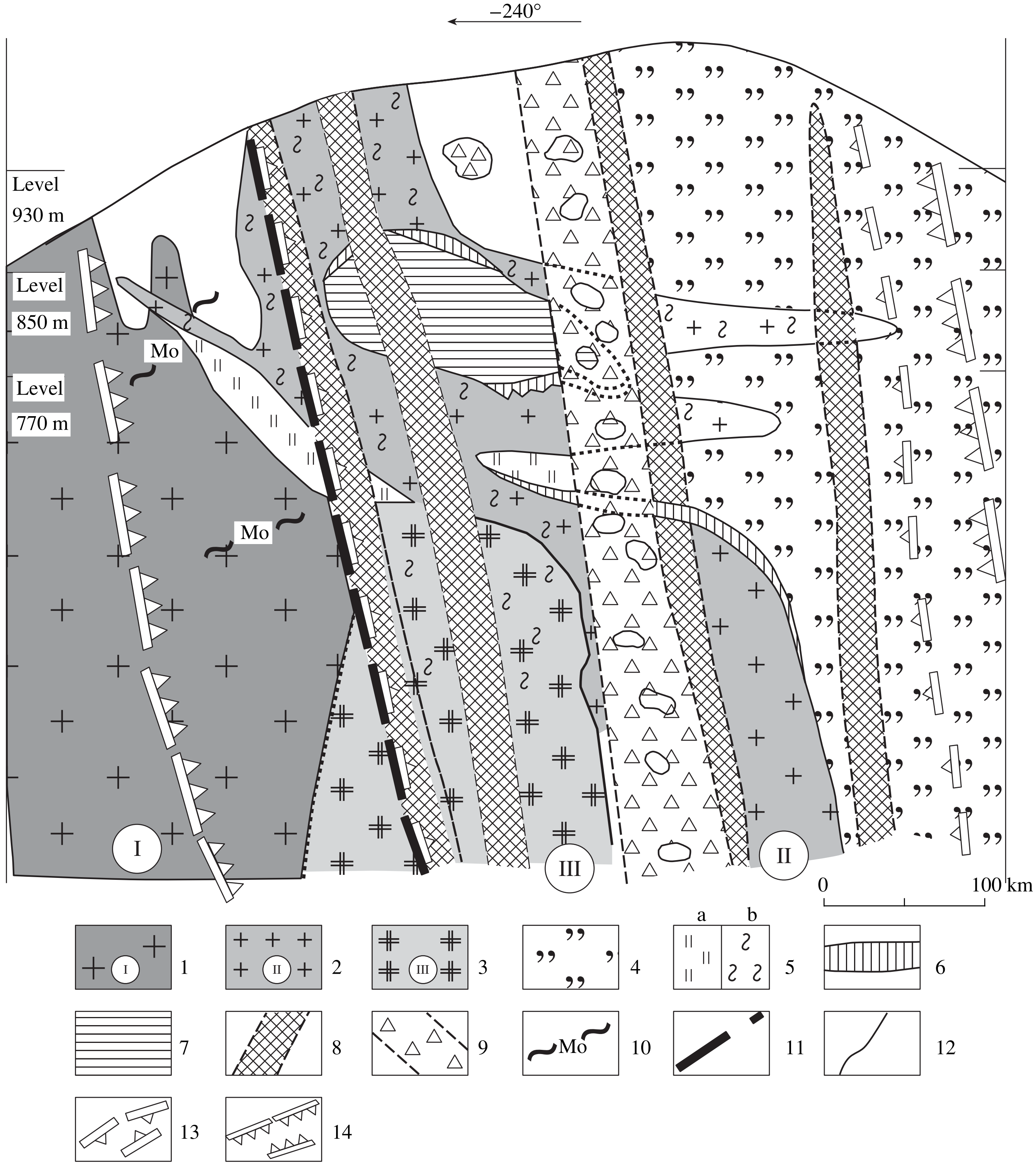

Fig. 3. Schematic geological section of the Tigrinoe deposit. (1) Granite–porphyries of the Bol'shoi stock (phase I); (2) medium-grained protolithionite–zinnwaldite granites of the Malyi stock (phase II); (3) porphyritic zinnwaldite granites with pea-shaped quartz (phase III); (4) quartz–biotite with siderophyllite and protolithionite hornfelses; (5) metasomatic rock alterations: silicification (a), greisenization (b); (6) stockscheider; (7) massive Sn-bearing greisens (Tigrenok lode); (8) projection of the zone of maximum development of ore veinlets (ore stockwork) on the section plane; (9) projection of the hydrothermal–explosive breccia body on the section plane; (10) quartz veinlets with molybdenite; (11) tectonic fractures; (12) boundaries; (13, 14) boundaries of ore mineralization: (13) tin–tungsten, (14) molybdenum.

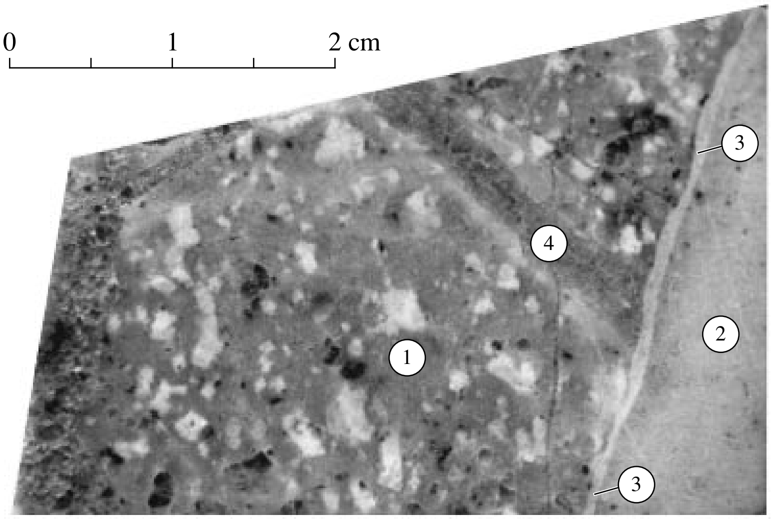

Fig. 4. Contact of the protolithionite–zinnwaldite granites of the Malyi stock (1) with granite porphyries of the Bol'shoi stock (2), cutting molybdenum-containing quartz veinlets of the pneumatolytic stage (4); (3) quenching zone.

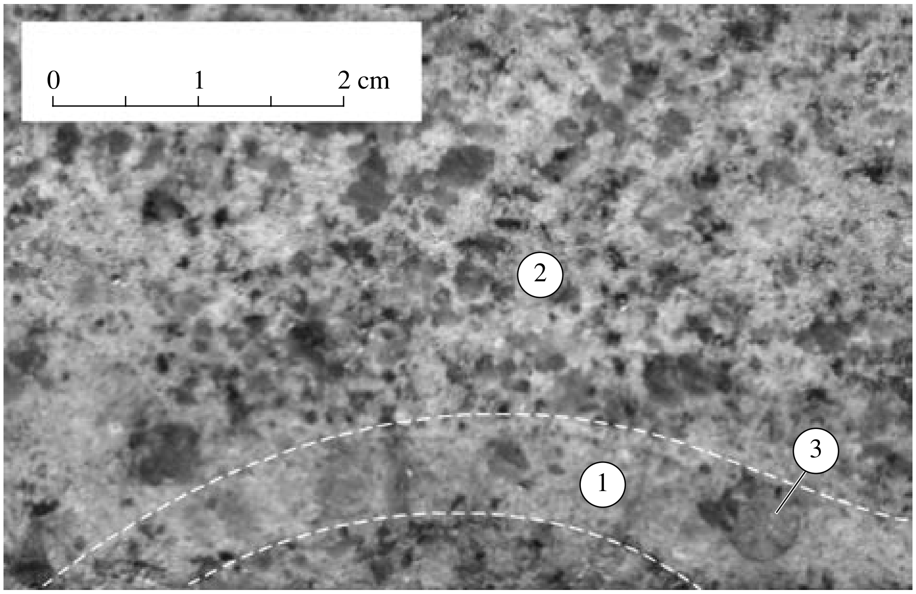

Fig. 5. Veinlet of porphyritic zinnwaldite granite of phase III (1) in medium-grained protolithionite–zinnwaldite granite of phase II (2); (3) pea-shaped quartz.

liest of them are granite–porphyries (porphyritic rhyolites) of the Bol'shoi stock. Borehole cores display their direct contact with the apophysis of the Malyi stock, which is made up of a fine-grained facies of medium-grained protolithionite–zinnwaldite (zinnwaldite) granites. The clearly defined quench zone suggests that, by the time of the Malyi stock emplacement, rocks of the Bol'shoi stock in the apical zone had been crystallized and had a relatively low temperature. The granite apophysis of the Malyi stock also cuts the quartz–molybdenite stringer crossing granites of the Bol'shoi stock (Fig. 4).

Conspicuous porphyritic (pea-shaped) granites of the Malyi stock, occurring at a depth of more than 200 m, represent the latest phase. The succession of phases is marked by veinlets of porphyritic granites in medium-grained protolithionite–zinnwaldites (Fig. 5), as well as linear zones of metasomatites (albitites) in the latter, which might be associated with the deeper seated porphyritic (pea-shaped) granites.

According to the chemical compositions, the granitoids described belong to the family of subalkalic leucogranites of the potassic–sodic series of the high-alumina Li–F geochemical type (Table 1). According to

Table 1. Chemical compositions of granitoids in the Tigrinoe depo

Components	Granite porphyries of the Bol'shoi stock; phase I (10)	Medium-grained granites of the Malyi stock; phase II (16)	Porphyritic granites of the Malyi stock; phase III (7)	Monzodiorites of Burelomnyi Creek (2)
wt %				
SiO_2	75.74	75.73	71.72	56.45
TiO_2	0.06	0.03	0.01	0.75
Al_2O_3	13.34	13.18	16.18	16.37
Fe_2O_3	0.20	0.17	0.23	1.21
FeO	0.55	0.60	0.55	6.03
MnO	0.01	0.03	0.09	0.15
MgO	0.13	0.10	0.12	5.63
CaO	0.48	0.45	0.36	6.13
Na_2O	4.00	4.13	5.87	2.87
K_2O	4.98	4.52	3.56	2.99
Li_2O	0.01	0.08	0.11	0.002
Rb_2O	0.05	0.13	0.12	0.01
P_2O_5	0.02	0.03	0.05	0.40
F	0.53	0.55	0.80	0.04
g/t				
Ni	7	4	3	190
Co	3	0.2	–	23
Cr	7	2	10	230
V	9	9	3	265
Cu	45	22	26	170
Sn	21	28	38	4
Pb	79	75	56	21
Zn	102	162	244	76
B	29	15	18	10
Mo	12	4	11	4
Be	5.9	6.8	5.0	1.8
Nb	50	55	86	21
W	32	53	302	3
Sr	22	40	18	155
Na_2O/K_2O	0.80	0.91	1.65	0.96

Note: The analyses were performed at laboratories of the Far East Geological Institute. "–," the concentration of the element is below the sensitivity of the analysis. The number of analyses is in parentheses.

the content of Al_2O_3, the agpaitic coefficient (Beus *et al.*, 1962), and the normative composition (Kovalenko, 1977), they may be assigned to amazonite–albite or microcline–albite varieties. In this case, granite porphyries of the Bol'shoi stock and rhyolite porphyries of dikes, least enriched in normative albite, are regarded as two- or monofeldspar leucogranites, whereas pea-shaped granites of the Malyi stock correspond to albite varieties. In the intrusive phases distinguished, the Na/K ratio naturally increases and the K/Rb ratio diminishes. From the first variety of granites to the third, the content of elements exceeding Clarke values that determine the ore potential—F, Li, Sn, Zn, W, Nb—increases and, in parallel, the content of siderophile elements decreases. Generally, these alterations agree with the assumption that granites were from successively emplaced, during the evolution of the ore–magmatic system, portions of rhyolite magma saturated with volatile components, in particular, fluorine. High and progressively increasing fluorine activity is demonstrated by the albite trend that occurred during the formation of successive intrusive phases of the magmatic evolution and alteration of the composition of granite micas and early postmagmatic mineralization (Gonevchuk and Gonevchuk, 1990).

The isotopic (K–Ar method) age of Bol'shoi stock rocks (Tomson *et al.*, 1996) is 92 ± 4 Ma. Age datings for the Malyi stock are numerous but rather controversial (Gerasimov *et al.*, 1990; Gonevchuk *et al.*, 1997; Rub *et al.*, 1986; Tomson *et al.*, 1996; Ishihara *et al.*, 1991). In our opinion, the age of the protolithionite–zinnwaldite granites of phase II is, most likely, 90 Ma, whereas zinnwaldite (pea-shaped) granites of phase (subphase) III are about 85 Ma. In addition to K–Ar and Rb–Sr dating, the age is confirmed by the Sm–Nd

Fig. 6. Quartz–feldspar and quartz–topaz–fluorite veins and veinlets in quartz–siderophyllite hornfels are accompanied by bleaching zones. Test pit, 1/4 natural size.

method (Belyatsky *et al.*, 1998). As reported by Rub *et al.* (1991), the Rb–Sr datings for the successive intrusive phases II and III are 73 and 67 Ma, respectively.

The available geological evidence suggests that monzonitoids of dikes and of the Burelomnyi Creek stock are pregranite, while the K–Ar method suggests that they are coeval (89 ± 4 Ma) with the early granitoid phase (Tomson *et al.*, 1996).

Latest ((27 ± 3)–(12 ± 0.4) Ma; Baskina, 1988) are dikes of subalkalic olivine basalts cutting all granites.

According to geological evidence, the age of mineralization is Late Cretaceous. Rub *et al.* (1986) dated the isotopic age of zinnwaldite and orthoclase as 86 ± 4 Ma. Our evidence (Gonevchuk *et al.*, 1987; Ishihara *et al.*, 1997) obtained by the K–Ar method on mica showed that the age of early vast (late magmatic) greisenization is close to that of protolithionite–zinnwaldite granites (phase II) and vein greisens formed (81 ± 4)–(78 ± 2) Ma.

POSTMAGMATIC ALTERATIONS

The ore mineralization of the deposit is represented by the molybdenum and tungsten–tin types localized in the two separate stockwork zones in voluminous greisens, at a bend of the Malyi stock and in the body of hydrothermal–explosive breccias. The early, molybdenum mineralization is confined to a system of east–northeast gently dipping (30°–40° SE) fractures in granite porphyries of the Bol'shoi stock and enclosing sedimentary rocks. Mineralization intensity falls to the east and southeast of the Bol'shoi stock, where the amount and thickness of Mo-bearing veinlets decrease.

The main ore-bearing (W–Sn) zone of the deposit is a linear stockwork (its strike is 315°–340°, and the inclination of the axial plane is 75° to the NE) composed of a thick net of parallel veinlets of different composition (Fig. 6) occurring in sedimentary and intrusive rocks. It is spatially linked with the Malyi stock (Figs. 2, 3). The stockwork extends along its strike for about 2000 m; its thickness amounts to 500 m. In sedimentary rocks, systems of veinlets and thin veins are traced along the dip for more than 1000 m, and their root zones, in most cases, reach granites of the Tigrinoe intrusive. Closer to the contact with granites of the Malyi stock, greisenization becomes more intense, producing massive quartz–topaz–mica or, in some cases, topaz or quartz–topaz greisens, with abundant disseminated ore minerals. The most intense greisenization (the Tigrenok ore occurrence) is assigned to the southern contact of the Malyi stock, where its high-angled inclination gives way to gentle dipping, having been cut by a pipelike body of hydrothermal explosive breccia (Fig. 3). The contacts of quartz–topaz–mica greisens with breccia display isometric segregations (about 2 m) composed of large-flaked zinnwaldite aggregates intergrown with fluorite. It is supposed that the pipelike body of breccias was a channel for arriving volatile components from deep zones. The distribution of greisens is restricted along both the strike and the dip.

At the upper levels, the body of hydrothermal–explosive breccia occurs among contact hornfelses and their fragments, cemented by vein quartz with occasional disseminations of sulfides (pyrrhotite, pyrite, stannite, and sphalerite). The tin mineralization here is poor. With depth (Adit 5, 850-m level; Fig. 4), the breccia penetrates into granites of the Malyi stock; there it

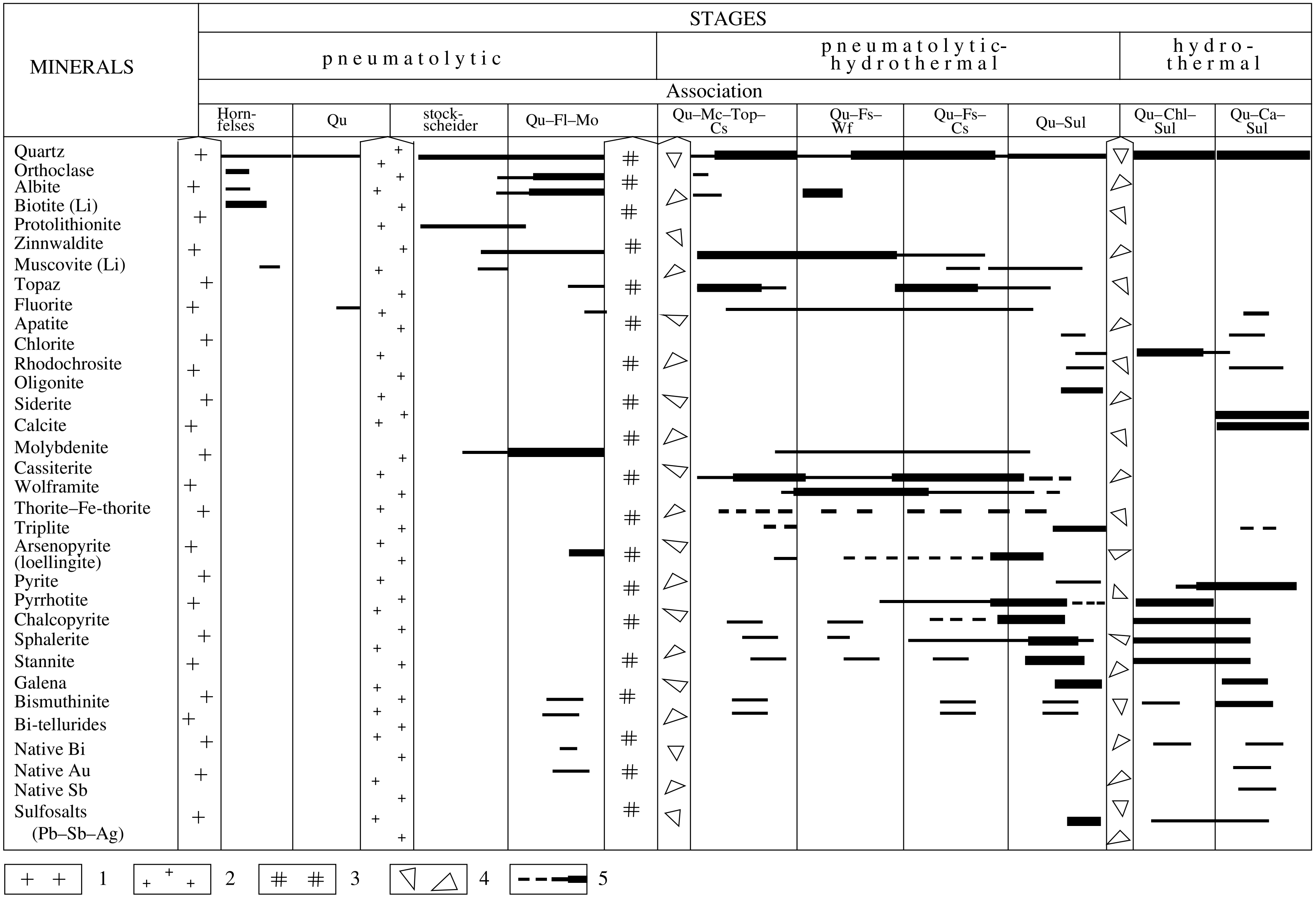

Fig. 7. Scheme of ore formation in the Tigrinoe deposit. (1) Granite porphyries (porphyry rhyolites) of the Bol'shoi stock, phase I; (2) medium-grained (upper) granites of the Malyi stock, phase II; (3) porphyritic (lower) granites of the Malyi stock, phase III; (4) explosive–hydrothermal breccia; (5) interval and intensity of the mineral phase formation. Minerals: Wf, wolframite; Ca, carbonates; Qu, quartz; Cs, cassiterite; Mo, molybdenite; Fs, feldspar (orthoclase); Mc, mica (zinnwaldite, muscovite); Sul, sulfides; Top, topaz; Chl, chlorite; Fl, fluorite.

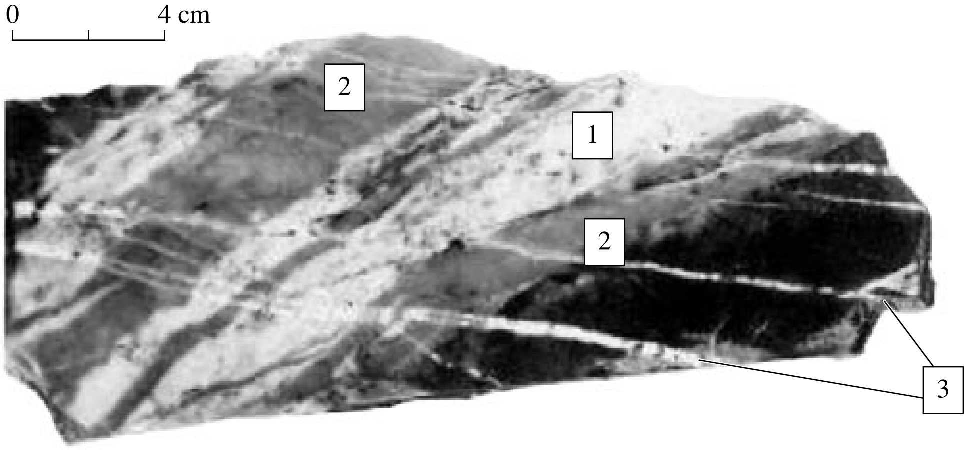

Fig. 8. Quartz–feldspar vein with small molybdenite aggregates (1) and bismuth minerals in bleached siderophyllite hornfels (2) crossed by thin quartz–topaz veinlets (3) with fine cassiterite disseminations. Sample, 1/2 natural size.

is composed of hornfels fragments; greisenized granites; and, partly, stockscheider, relicts of which are preserved in rims of granite bodies. In this zone, the mineralization is mainly concentrated in breccias, where cassiterite or, in lesser amount, arsenopyrite and stannite, associated with quartz and subordinate zinnwaldite and topaz, make up the cement.

Crosscut no. 47 (Adit 7, 770-m level) revealed in the outer border of granites a thick zone of feldspar metasomatites, which, splitting into small veinlets, passes into granites, where it is accompanied by rich cassiterite mineralization.

Based on geological, mineralogical, and isotopic–geochronological investigations, three stages are distinguished in the deposit formation: pneumatolytic (syn-, late-, and postmagmatic), pneumatolytic–hydrothermal, and hydrothermal; each of them is represented by several mineral associations (Fig. 7).

Pneumatolytic Stage

High fluid saturation of the melt during the emplacement of the Tigrinoe intrusive accounts for intense processes of contact–metasomatic transformation of host rocks, whereas relatively low temperature and predominance of the F and Li volatile components in the composition favored a subgreisen type of alterations. It is most typical of the exocontact metasomatites of the Malyi stock, composed of granites of the final, most F-enriched phases. In these peculiar "hornfelses," represented by fine-grained aggregates of quartz, fluorite, feldspar, and topaz and fine-flaked Li-containing mica, the Zn concentrations are recorded at a level of 300 g/t; Mo, 40 g/t; and Sn, 25 g/t. As was mentioned above, silicification of host rocks mostly occurs in exocontact zones of the Bol'shoi stock. This mineralization, like stockscheiders and quartz–feldspar metasomatites, similar to them in composition, may certainly be regarded as synmagmatic pneumatolytic. However, with regard to structural and lithologic isolation, the earliest syn- and postmagmatic pneumatolytic association is considered to be the quartz assemblage paragenetically associated with granitoids of the Bol'shoi stock. Small, W–E oriented quartz veins and veinlets with scarce molybdenite flakes and slightly colored fluorite grains were localized in the hornfelses and granitoids of the Bol'shoi stock and are cut by granites of the Malyi stock, as well as by veins and veinlets of the linear ore stockwork (Fig. 4).

The formation of the quartz association was interrupted by the emplacement of the medium-grained protolithionite–zinnwaldite granites of the Malyi stock and concurrent stockscheiders. The quartz–feldspar–molybdenite mineral association developed simultaneously (but prior to greisens). It is represented by a dense net of gently dipping (30°–40° to the SE) veins and veinlets of quartz and quartz–feldspar composition with molybdenite, bismuthinite, native bismuth, bismuth tellurides, and gold (Fig. 8). These veins and veinlets cross the Bol'shoi stock and spread eastward in hornfelses and stockscheiders. In granites of the Malyi stock, mineralization sharply disappears.

The pneumatolytic stage was completed with the introduction of the porphyritic (pea-shaped) granites of phase III and later formation of the pipelike body of explosive–hydrothermal breccia.

Pneumatolytic–Hydrothermal Stage

The formation of the complex W–Sn ores (essential ores of the deposit) at the pneumatolytic–hydrothermal stage commenced with the development of the greisen—*quartz–mica–topaz (with cassiterite)*—association, most conspicuous near the southern contact of the Malyi stock, at the place of its convergence with the body of explosive–hydrothermal breccias. According to the dominating minerals, quartz, mica, and topaz greisen varieties are distinguished. The ore mineralization in them is represented by evenly disseminated cassiterite; sphalerite; stannite; wolframite; and, in a lesser amount, arsenopyrite. Cassiterite prevails in topaz-enriched zones. Greisens are dissected with quartz veinlets and veins with abundant sphalerite, stannite, and zinnwaldite rims. As the intensity of greisenization of granites falls, quartz veins and veinlets with topaz and zinnwaldite appear in them, with abundant dissemination and nests of cassiterite; wolframite; and, in a lesser amount, molybdenite, arsenopyrite, sphalerite, and stannite. These veins for the first time showed the presence of thorite and triplite.

The following mineral associations are identified in the linear ore-bearing stockwork within the pneumatolytic–hydrothermal stage.

The quartz–feldspar orthoclase association with wolframite and cassiterite is widespread in the stockwork zone among exocontact hornfelses of the Malyi stock, which were transformed into dark mica greisens (zvitters) and hosted dikes of porphyry rhyolites. It is less abundant in greisenized granites. These veins and veinlets are characterized by a symmetric zonal structure: the axial parts are essentially composed of feldspar, the next zone is made up of equigranular quartz, and selvages are filled with zinnwaldite. According to composition, ore minerals are distinguished as:

—virtually ore-free quartz–feldspar veinlets in hornfelses, in some cases, with disseminated fluorite, topaz, and small disseminated zinnwaldite flakes;

—quartz–feldspar veinlets with disseminated topaz and wolframite, the selvages of which are rimmed with large-flaked zinnwaldite; sporadic small nests of arsenopyrite and bismuth minerals are confined to the quartz zones of veinlets, while stannite and sphalerite occur in the axial (feldspar) zone;

—quartz–feldspar veinlets and veins with cassiterite and wolframite dominate; they are commonly accompanied by large-flaked zinnwaldite rims comparable with the thickness of the veins themselves; wolframite is commonly confined to the areas enriched in feldspar, and cassiterite, to the zones rich in quartz; wolframite–cassiterite intergrowths are rare, even in the same vein; if they are encountered, they are confined to longitudinal fractures filled with quartz and topaz;

—quartz–feldspar–mica (with cassiterite, fluorite, and sulfides) veinlets and small veins are scarce; in some cases, they have a symmetric zonal structure: selvages contain feldspars with a small amount of mica followed by quartz zones with mica and cassiterite, while the axial part, in addition to quartz, displays aggregates of light violet fluorite and sparse sphalerite and stannite dissemination.

The wolframite–quartz and cassiterite–quartz mineral associations have a subordinate distribution in the ore-bearing stockwork. Only small veins are encountered, in hornfelses and greisenized granites, where cassiterite with wolframite, occasionally with molybdenite, forms nests isolated in vein quartz.

The quartz–sulfide mineral association is represented by numerous veins and veinlets in hornfelses and in greisenized granites. Sulfides (sphalerite, stannite, and occasionally chalcopyrite) and sulfide-corroded grains of cassiterite or wolframite are disseminated in them or form nests in the central part, and selvages show the presence of mica and topaz rims with a thickness ranging from fractions of a millimeter to 20 cm. In these veinlets, arsenopyrite and loellingite cement cataclastic grains of wolframite and cassiterite. In many cases, quartz–sulfide veins and veinlets, which dissect quartz, quartz–feldspar, wolframite–quartz, and cassiterite–quartz veins, as well as greisens and greisenized granites, exhibit sulfide nests intergrown with cassiterite and wolframite without visible signs of crushing of the latter. We suggest that their formation was close in time. This association is characterized by a wide development of phosphates, sulfides, and sulfosalts (Fig. 7).

Hydrothermal Stage

The hydrothermal *quartz–chlorite–sulfide mineral association* occurs at the flanks of the ore-bearing stockwork where it penetrates contact hornfelses of the biotite–chlorite and chlorite facies. The association is represented by thin quartz veins and veinlets and by thin bands of quartz that contain nests and disseminations of sulfides and sulfosalts, dominated by pyrrhotite, sphalerite, chalcopyrite, stannite, and pyrite developing after pyrrhotite. Veinlet rims are made up of fine-flaked light green thuringite-type chlorite. This mineral association is, evidently, a facial variety that accumulated during the pneumatolitic–hydrothermal stage of the quartz–sulfide association.

The quartz–carbonate–sulfide mineral association is of subordinate distribution. Independent carbonate-containing quartz–pyrrhotite–chalcopyrite–sphalerite–galena veinlets were identified outside the ore-bearing stockwork in the northern part of the deposit. The association is widespread in the upper levels of the explosive–hydrothermal breccia, where interstices in quartz that cemented fragments are filled with carbonate–sulfide–fluorite aggregates. The sulfides are represented by arsenopyrite, sphalerite, stannite, and pyrrhotite, as well as by substituting pyrite, marcasite, and magnetite. Locally, pyrrhotite occurs in association with tabular aggregates of Ag and Bi sulfosalts. In such places, carbonates are combined with manganese phosphates.

The oxidation zone, marking the supergene stage of the deposit formation, is a blanketlike cover, 40–80 m thick. The chemical oxidation of primary ores proceeded through decomposition of primary sulfides and formation of supergene minerals, dominated by varlamoffite (replacing stannite), ferric hydroxides, and several other minerals. A relatively small thickness of the oxidation zone is accounted for, on the one hand, by weak postore tectonics and, on the other hand, by a high erosion rate, higher than that of weathering. In these

Table 2. Mineral compositions of ores of the Tigrinoe deposit

Essential	Accessory	Rare
	Hypogene	
	Ore	
Cassiterite, wolframite, sphalerite, stannite, arsenopyrite, molybdenite	Loellingite, pyrrhotite, chalcopyrite, pyrite, marcasite, galena, bismuthinite, bismuth, gustavite-lillianite, Ag-bearing cosalite	Magnetite, joseite A, Se-joseite B, heyrovskite, Nb-bearing rutile, rutile, native silver*, scheelite, Hf zircon*, thorite*, ferrithorite*, xenotime*, columbite*, W-ixiolite*, tapiolite*
	Vein	
Quartz, topaz, K-feldspar, albite-oligoclase, zinnwaldite, Li-biotite, fluorite	Protolithionite, Li-muscovite-phengite, rhodochrosite, oligonite, apatite, kaolinite, triplite	Chlorite, sericite, calcite, triploidite, eosphorite
	Supergene	
Varlamoffite, ferric hydroxides	Scorodite, covellite, greigite	Chalcocite, bornite, cuprite, malachite

* The minerals were identified by Rub *et al.* (1998).

conditions, only the initial stage of weathering crust is preserved, with a small amount of clay material. It can be assumed that, in more ancient epochs, the conditions were more favorable for the formation of weathering crust, which, when washed out, formed small-scale cassiterite placers in nearby valleys.

The mineral types and varieties described from mineral associations do not embrace the entire variety of ore and vein minerals of the deposit. The list presented by Popov and Popova (1992) includes 150 minerals. A somewhat smaller number of minerals is given in the work by Ruchkina *et al.* (1986). Nevertheless, not all of them were reliably diagnosed and not all were confirmed by other researchers. The list of well-documented minerals amounts to 59 (Table 2), though, in our opinion, it is not complete.

The ore complex in the Tigrinoe deposit is determined not only by the diversity of mineral forms of ore assemblages but also by the presence of disseminated elements. Analysis of the distribution of accessory components in ores and minerals (Table 3) indicated that, in addition to Sn and W, which are the most valuable elements of the deposit, there are significant rare and disseminated metals (Ta, Nb, Sc, In, Ag, Bi, Cd, and others) contained in cassiterite, wolframite, stannite, and sphalerite. Ores include appreciable amounts of thorite and ferrithorite.

FORMATION CONDITIONS OF THE ORE–MAGMATIC SYSTEM

The authors investigated the genesis of the ore–magmatic system of the Tigrinoe deposit assuming that the initial fluorine activity was high, being, most likely, caused by involvement of a deep fluid in the magma- and ore-forming process. This is confirmed by some “mantle” ratios of strontium and neodymium isotopes (Belyatsky *et al.*, 1998); oxygen, in granites; and sulfur, in ore minerals of the early pneumatolytic stage. The participation of deep-seated matter in the genesis of the deposit is indirectly confirmed by a persistent presence of tellurium (Bi tellurides, to be more precise) in the composition of ore minerals, which Sakharova *et al.* (1998) regard as an indication of a deep origin of ore-bearing solutions. This is also supported by the presence of monzonites that are located not far away (about 4 km) from the deposit and are, in fact, coeval with granites, as well as by subalkalic basalts localized directly in the ore field; Baskina (1988) reliably proved their mantle genesis.

The changes in compositions of the Tigrinoe massif intrusive phases can be properly explained by the model of melting out of successive portions of silicate melt from the metamorphic substrate under constant or slightly decreasing temperature and increasing fluorine activity. In this case, extension of the quartz crystallization field and the albite-enriched eutectic (Bogolepov and Epel’baum, 1987) may be due to the diminishing of the silica content and increasing of the Na/K ratio in the period from the first to the third phase accompanied by the formation of an albite trend. The results of a statistical analysis of granitoids in the Tigrinoe deposit (Gonevchuk and Gonevchuk, 1991) suggested that this relationship of components is recorded by a notable positive correlation of Na_2O and Li_2O and a negative correlation of K_2O and SiO_2 with fluorine.

On the whole, the formation of the ore-bearing granitoid association may be presented as follows:

—intrusion of magmatic (rhyolite) melt, the predecessor of granite porphyries of the Bol’shoi stock and, probably, of rhyolite porphyric dikes;

—intrusion of more low-temperature and Li- and F-saturated granite melt of the Malyi stock.

This was followed by differentiation of melts in separate “microchambers.” In the Bol’shoi stock, where the conditions were unfavorable for differentiation of melts (near-surface intrusion), the process was completed by the isolation of intergranular (eutectoid) K-enriched melt over restricted zones. In the Malyi

Table 3. Distribution of accompanying components in ores and minerals of the Tigrinoe deposit

Ore, mineral	Li_2O	Rb_2O	Zn	Pb	Cu	Mo	Ag	Bi	Sb	In	Cd	Sc	Nb_2O_5	Ta_2O_5
	wt %			g/t										
Veinlet-disseminated ore (150)	0.5	0.4	0.77	130	530	73	20	100		50	20	50	30	10
Greisen ore (150)	1.44	0.38	1.46	30	740		5	90		90	80	110	45	10
Cassiterite (15)										$\frac{30–180}{90}$		$\frac{460–730}{598}$	$\frac{260–1720}{1061}$	$\frac{10–150}{52}$
Wolframite (25)												$\frac{360–3400}{1742}$	$\frac{830–12500}{4390}$	$\frac{60–290}{82}$
Sphalerite (26)							$\frac{40–300}{80}$	$\frac{\text{Traces}–400}{60}$		$\frac{430–6810}{3188}$	$\frac{1780–3410}{2764}$			
Stannite (13)							$\frac{\text{Traces}–880}{401}$	$\frac{10–190}{82}$		$\frac{210–1130}{472}$	$\frac{420–1120}{897}$			
Loellingite (2)							Traces	$\frac{600–790}{695}$	Traces					
Arsenopyrite (13)							$\frac{10–50}{12}$	$\frac{80–1550}{536}$	$\frac{90–5120}{650}$					
Pyrite (1)							110	680	150					
Galena (3)*							1300	41200	1100					

Note: The number of analyses is given in parentheses; the ultimate concentrations, in the numerator; the average content, in the denominator. The chemical analyses were performed using duplicates of samples (analysts, V.N. Zalevskaya, G.I. Gorbach, and L.S. Levchuk, Far East Geological Institute, Far East Division, RAS (FEGI RAS). * Microprobe X-ray spectroscopy analysis (analysts, V.I. Sapin and A.P. Nedashkovskii, FEGI RAS). JXA-5A microprobe. Conditions of the analysis: tension, 25 kV; probe current, 60 nA.

stock, the initial melt of which (intruded later) was enriched in Li, F, and water and, judging by mineral associations (Gonevchuk and Gonevchuk, 1990; Korostelev *et al.*, 1990), became increasingly rich in volatile components in the course of evolution due to their influx from deep zones, the differentiation was more complete. This led both to the development of the above-described granitoid phases of the stock ("outer" and "inner" granites in the models of Rundquist *et al.* (1971) and to the evolvement of two chambers of ore–magmatic residual, conforming to the model of crystallization of melt rich in volatile components (Tauson, 1989). It is their evolution that could account for the formation of large-scale and linear greisen bodies. "Explosive brecciation" in such a model could mark the stage of catastrophic discharge of the lower chamber. Such breccias are known in most deposits associated with Li–F granites.

Specific features of magmatism development are emphasized by the compositions and interrelations of "ore-forming" mineral associations and by the behavior during their formation of petrogenetic and ore-generating elements that may be derived from different phases of magmatism. The formation of quartz–feldspar hornfelses, which contain Li- and F-rich biotite, was concurrent with the early phase of granite–porphyries of the Bol'shoi stock. The process of hornfels formation ended in development of quartz (quartz–molybdenite) veinlets and voluminous metasomatites, which created a huge (about 1 km) halo in the eastern and northeastern endo- and exocontacts of the stock.

The emplacement of the Malyi stock, enriched in volatile components, Li and F in particular, was accompanied by the development laterally of stockscheider zones bearing molybdenite. The formation of molybdenite–quartz–feldspar veinlets, replacing quartz ones, also occurred in that period. A deep-seated chamber of earlier developed granite porphyries may have served as a molybdenum source. This was confirmed by the isotope composition of sulfur of molybdenites. Probably, in that period, at a crossing of variously oriented tectonic fractures, there was formed a structure that was intruded up to the 850-m level by granites of the Malyi stock that, subvertically dipping at this interval, higher up gave way to a more gentle dip. Further, the structure accounted for the localization of the hydrothermal–explosive breccia.

The emplacement of phase III—"inner granites" of the Malyi stock (with pea-shaped quartz)—was accompanied by active arrival of volatile and ore-generating components and led to the formation of voluminous greisens and a linear W–Sn stockwork. The formation of voluminous greisens was assigned to the bend in the Malyi stock, where the subvertical dipping changed to a more gentle one. It occurred concurrently with an increase in volatile contents in the structure of the hydrothermal–explosive breccia. This is confirmed by intensifying greisenization near the breccia body and by the presence in it of hornfels fragments reworked into fine-laminated rocks and cemented with a topaz–mica–quartz substance containing cassiterite, wolframite, arsenopyrite, and fluorite.

Further evolution of the ore-bearing center, accompanied by a drop in temperature and pressure, led to the change of pneumatolytic and pneumatolytic–hydrothermal solutions for hydrothermal ones, which promoted the deposition of large amounts of diverse sulfides and sulfosalts. At the same time, the share of upper crustal matter in the composition of ore-forming solutions increased. It affected, in particular, the S isotopic composition, which became somewhat lighter. The pneumatolytic–hydrothermal stage was accompanied by considerable deposition of ore minerals, among which, in addition to cassiterite and wolframite, were sulfides, sphalerite, and stannite; arsenopyrite and molybdenite were less abundant, and chalcopyrite and galena were sporadic. We suggest that molybdenite in this case was redeposited. The end of the pneumatolytic–hydrothermal stage coincided with the final period of the hydrothermal–explosive breccia formation. In this period, fragments of greisens and stockscheider appear in its composition in addition to fragments of hornfelsized host rocks, which predominate. Quartz with a small amount of sulfides, carbonates, and fluorite served as a cement. No appreciable shifts of detrital material were observed in the zone of breccias in that period. This means that the completion of the ore process was rather calm.

The pneumatolytic–hydrothermal stage was replaced by the deposition of quartz–chlorite–sulfide and quartz–carbonate (calcite)–sulfide veinlets of the hydrothermal stage.

Isotopic datings suggest a relatively short-term evolution of the ore–magmatic system. The emplacement of the outer and inner granites of the Malyi stock and processes linked with them are close in time (80 ± 3 Ma (Belyatsky *et al.*, 1998); 73.2 ± 0.2 and 67 ± 2 Ma, respectively (Rub *et al.*, 1998)). Within the accuracy of the analysis, the K–Ar and Sm–Nd age datings for zinnwaldite, fluorite, and wolframite mark these processes. This is also indicated by the similar hydrogen isotope composition in micas of different ore-forming stages. A certain distinction between the isotopic composition of early molybdenite sulfur (δ^{34}S +1.34–+1.65‰) and its composition in sulfides of the pneumatolytic–hydrothermal and hydrothermal stages (δ^{34}S −1.1…–4‰) may emphasize the time difference between the earliest ore-formation stage, associated with the emplacement of phase I granitoids, and the following stages and the closer relation of that stage to magmatism.

Isotopic geochemistry data confirm the magmatic nature and common source of ore-forming fluids. However, the identified presence of magnesium in the composition of gas–liquid inclusions in the quartz of ore veinlets with predominant K, Na, and Ca chlorides

(Pakhomova *et al.*, 1992) indicates the involvement in the process of more basic (than granites) sources of ore-forming solutions. As reported by these authors, there is a clear difference between the fluid regime of formation of the granite porphyries in the Bol'shoi stock (phase I) and the average-grained granites (phase II) in the Malyi stock. The fluid phase in melt inclusions of the Bol'shoi stock occupies 5–7% of the volume; that in melt inclusions of the Malyi stock, 10–15%. The composition of the fluid phase of melt inclusions of Malyi stock granitoids marks lower K and increased Na, Li, and F significance, which agrees with the changing composition of its phases. The homogenization temperatures of these inclusions in the Bol'shoi stock are 970–990°C; in the Malyi stock, 880°C.

The silicate melt inclusions in quartz of the Bol'shoi stock granites contain one or two solid phases and a fluid, whereas the granites of the Malyi stock, which contain a much greater amount of such inclusions, consist of three to four solid phases, two of which are sylvite and gallite, and a fluid. When heated, such inclusions are disclosed at a temperature of about 700°C.

Investigations of fluid inclusions showed that the formation of postmagmatic rocks (Kokorin and Kokorina, 2003) proceeded under conditions of a progressive drop in temperature, pressure, and concentration of salts and gases in the solution:

—the maximum temperature (650–150°C) and pressure (1000–200 bar) at a concentration of CO_2 up to 35 wt % and of salts up to 60 wt %-equiv NaCl were established for quartz inclusions of the earliest quartz association of the pneumatolytic stage;

—molybdenite-bearing quartz–feldspar veins and veinlets of the pneumatolytic stage, accompanying the emplacement of the Malyi stock, formed at a temperature of 560–150°C, a pressure of 800–150 bar, and a concentration of CO_2 in the inclusions of about 30 wt % and of salts of about 50 wt %-equiv NaCl;

—the deposition of the main productive mineral associations of the pneumatolytic–hydrothermal stage was recorded by temperatures of 450–75°C with an increase in CO_2 concentration to 60 wt % and a drop in the concentration of salts to 20 wt %-equiv NaCl;

—the minimum values of temperature (300–50°C) and pressure (250–100 bar), a lack of CO_2, and concentration values of salts of about 25 wt %-equiv NaCl are characteristic of mineral inclusions of the final hydrothermal stage.

During the formation of the hydrothermal–explosive breccia, the pressure in the ore-bearing system was, evidently, over 1000 bar.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-05-65270, and by the program of the Division of Earth Sciences, RAS, project no. 04-1-ONZ-111.

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