ISSN 0869-5911, Petrology, 2006, Vol. 14, No. 4, pp. 413–420. © Pleiades Publishing, Inc., 2006.
Original Russian Text © R.L. Melkonyan, M.S. Akopyan, 2006, published in Petrologiya, 2006, Vol. 14, No. 4, pp. 439–448.

Some Aspects of the Interrelations between Magmatism and Ore Formation: Evidence from Oxygen Isotope Data on Ore–Magmatic Systems, Armenia

R. L. Melkonyan and M. S. Akopyan

Institute of Geological Sciences, Academy of Sciences of Armenia, pr. Marshala Bagramyana 24a, Yerevan, 375019 Armenia
e-mail: ramelk@sci.am

Received June 29, 2005

Abstract—The results of oxygen–isotope study of the Kokhb–Shnokh (J_3) and Vokhci (N_1) intrusive complexes and the related Tekhut and Kadzharan Cu–Mo porphyry deposits of different types, Armenia, were used to discuss the relevant problems of rock and ore genesis and their relationships. It was established that the assimilation of parental mantle basaltic melts by crustal, mainly feldspathic material is a decisive factor in the formation of multiple gabbro–granite complexes. Specifics in the composition and crystallization of the hybrid melt causes the enrichment of the residual melt and hydrothermal fluids in Fe and other elements, in particular, Cu and Mo. The ore-bearing solutions are generated over the solidification time of the melt. They are removed by the hydrothermal system of directionally moving solutions, a process that gives way to a convective–circulation hydrothermal system. A change in the spatial position of the hydrothermal solutions during the formation of the deposit supplies them to different sites, creating a seeming discontinuity in ore deposition, which is observed at many deposits. In fact, the supply of the ore-bearing solutions is continuous process. The ore stage is not a time interval with particular ore-bearing solutions but rather a certain physicochemical state of the solutions attained during their interaction with the environment. This process resulted in the simultaneous precipitation of different mineral assemblages and the asynchronous precipitation of the same assemblages. The formation of deposits of various metals related to a common intrusive complex, as changes in the composition of mineral assemblages, is caused by the influence of various geochemical barriers rather than by compositional variations in the initial hydrothermal solutions.

DOI: 10.1134/S0869591106040059

INTRODUCTION

The relationship between magmatism and ore formation remains one of the burning and fundamental geological problems for many decades. Although various aspects of this problem were studied by many geologists cursorily or in detail, no satisfactory solution has been offered as of yet.

A wide application of isotope methods over the last 25–30 years made it possible to obtain principally new information, which sometimes provides an unambiguous solution for some controversial problems. We studied various ore-magmatic systems in Armenia with Cu–Mo, Fe, and Au mineralization for two decades as examples of relationships between granitoid magmatism and ore mineralization. This work is based on isotope, primarily oxygen isotope, as well as geologic–petrographic and mineralogical–chemical data on some ore-magmatic systems. Oxygen isotope data are typically utilized to identify the genesis of rocks. In our research, these data were additionally applied to decipher the mechanism of the formation and operation of the ore-magmatic systems by comparison of the results obtained for different stages of a single process. The data thus obtained allowed us to illuminate in a new way some important issues of the discussed problem.

ROLE OF THE GENESIS OF THE GABBRO–GRANITE COMPLEXES IN THEIR ORE POTENTIAL

This problem is exemplified by the Mesozoic (Upper Jurassic) Kokhb–Shnokh island-arc ore–magmatic system, which consists of the Kokhb–Shnokh intrusive complex, the Tekhut Cu–Mo deposits, and small Fe deposits.

The Kokhb–Shnokh intrusive complex is a part of multiple tonalite (gabbro–tonalite) suite of the Mesozoic Pontides–Transcaucasian ensialic island arc and comprises small gabbroid, quartz diorite, tonalite, and granodiorite massifs extending from the Pontides through the Lesser Caucasus to Elburs. These intrusions are accompanied by Fe, Cu–Mo, base-metal, and other deposits and numerous occurrences of ore mineralization.

The Kokhb–Shnokh intrusive complex (~90 km^2 in area) includes three phases. The first phase occupies >90% of the area and is made up mainly of tonalites and

Table 1. Oxygen isotope composition of the rocks and minerals of the Kokhb–Shnokh intrusive complex

Rock	$\delta^{18}O$, ‰ (SMOW)				
	Rock	Quartz	Plagioclase	Orthoclase	Magnetite
Quartz diorite (I phase)	+7.1	+6.8	+8.2	–	–1.7
Pegmatite (II phase)	+8.1	+7.1	–	–	–1.7
Vein granite (II phase)	+8.1	+7.2	–	–	–1.5
Leucocratic granite (III phase)	+8.5	+7.5	+8.8	9.3	–1.0

Note: Oxygen isotope composition was determined at the Laboratory of Isotope Investigations, Institute of Geological Sciences, Academy of Sciences of Armenia, on a modernized MI-1201 mass spectrometer by the uncompensation method; the analytical errors were ±2‰.

quartz diorites with subordinate diorites and granodiorites. The rocks of the subsequent phases, pegmatites, granite porphyry, aplites, and leucocratic granites, compose small dike and stock-like bodies. These rocks are thought to be generated either by crustal assimilation or the crystallization differentiation of the parental basic melt. Different mechanisms give different isotope effects. During differentiation, equilibrium in the melt is disturbed with decreasing temperature, after which the system approaches new equilibrium. Since there was no disturbance in the isotope balance of the system, the opposite isotope effects should arise, i.e., an increase in the concentrations of the heavy oxygen isotope in some minerals should be accompanied by the lightening of the isotope composition of others. The formation mechanism of multiple granitoid intrusions can be unambiguously deciphered from oxygen isotope variations in quartz and magnetite within a single rock series (Akopyan and Melkonyan, 1986, 1981). The oxygen isotope fractionation between quartz and major rock-forming mineral under decreasing temperature leads to a heavier isotope composition of quartz, while fractionation between magnetite and other minerals results in the lightening of the oxygen isotope composition of magnetite.

The opposite effects should be caused by assimilation or mixing. In this situation, the isotope equilibrium is disturbed by the supply of the material with different oxygen isotope composition in a melt. Naturally, the influx of acid upper crustal material with heavier oxygen isotope composition causes a heavier isotope composition of the corresponding minerals of the melt and the disturbance of the equilibrium. A tendency toward equilibrium might lead to the distribution of heavy oxygen between other rock-forming minerals, including quartz and magnetite, and, respectively, to their heavier oxygen isotope composition.

Thus, if the formation of multiple granitoid complexes was controlled by mainly crystallization differentiation, the oxygen isotope composition becomes heavier for quartz and lighter for magnetite from early to late phase, whereas assimilation or mixing should result in a heavier oxygen isotope composition in quartz and magnetite.

The oxygen isotope study of the rocks from different phases of the Kokhb–Shnokh intrusion and major rock-forming minerals (Table 1) unambiguously suggests the assimilation mechanism. Quartz is known to have the heaviest oxygen isotope composition among equilibrium minerals. The heaviest isotope composition of feldspars testifies in this situation to disequilibrium crystallization and a predominantly feldspathic composition of the assimilated material. Previous petrographic–mineralogic and geochemical investigations also showed that the rock series from quartz diorites to leucocratic granites was formed by the assimilation of basaltic melts mainly by feldspathic material in an intermediate chamber (Meliksetyan and Melkonyan, 1976). The initial $^{87}Sr/^{86}Sr$ ratios in the rocks of different phases (0.70405 ± 0.00013 in I phase, 0.70458 ± 0.00027 in III phase) indicate an upper mantle source of the parental melt, while the shift in ε_{Sr} from negative values (–3.72) in the rocks of phase I to positive values (+3.67) in the leucocratic granites of the III phase also supports the crustal contamination of the melt (Melkonyan and Gukasyan, 2004).

Crustal assimilation results not only in compositional changes but also in the disturbance of the chemical and isotope equilibrium and the initiation of processes aimed at the attainment of a new equilibrium. According to Le Chatelier's principle, an increase in the content of the feldspathic component in the melt activates processes that lead to a decrease in the concentration of the assimilation component. This can be attained only by the crystallization of feldspars. Naturally, feldspars were the first to crystallize in all of the rocks (Meliksetyan and Melkonyan, 1976). In spite of the upper mantle source and basaltic composition of the parental melt, no high-temperature Fe-bearing mafic minerals crystallized, with the only exception of minor amounts of hornblende and biotite (no more than 7%), which formed after plagioclase of the first generation. This promoted iron enrichment in the residual liquids. The Fe-rich hydrothermal solutions produced both the Fe and Cu–Mo deposits of the Kokhb–Shnokh ore–magmatic system. The presence of Fe in the melt explains the accumulation of other metals (Cu, Mo, Zn, and Pb) typical of this ore-magmatic system. The Clarke value of Fe in intermediate rocks is almost

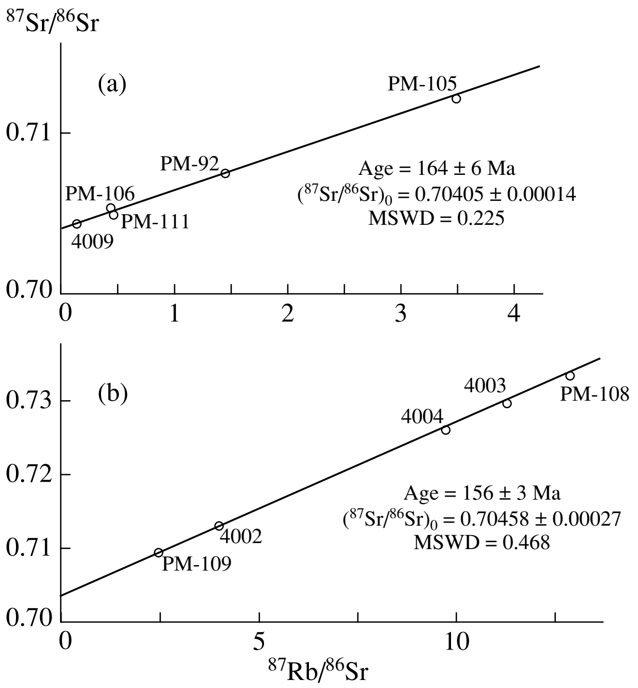

Fig. 1. Rb–Sr diagrams for rocks from various phases of the Kokhb–Shnokh intrusive complex.

(a) I phase: (4009) quartz diorite, (PM-106) tonalite, (PM-111) tonalite, (PM-92) quartz–biotite–feldspar facies pegmatite in tonalites, (PM-105) granite.

(b) III phase: (PM-109) leucogranite, (4002) granite, (4004) leucogranite with pegmatoid quartz–feldspar aggregates, (4003) aplitic leucogranite, (PM-108) leucogranite with pegmatoid pockets.

500 times higher than that of the aforementioned metals. Hence, if Fe is not incorporated in silicate minerals, it is accommodated in iron sulfide according to the law of mass action during differentiation. In view of the limited sulfur content in the melt, less abundant metals are mainly deprived of the possibility to form sulfides. They are accumulated in the residual products and are removed later with the fluid phase (Aslanyan et al., 1990).

The parental melt and assimilated material formed at different depths, i.e., under different redox conditions. During their interaction, the conditions changed both in the melt and in the assimilated material. This also can serve as an ore-mobilizing factor, since a change in the valence of ore-forming elements prevents the formation of ore minerals in the source and facilitates their escape with a fluid phase. No extraordinary processes are required to generate the ore potential of the Kokhb–Shnokh, as also follows from isotope data on other elements for various regions (Pushkarev, 1997; Hedge, 1977). It should be noted that the ore-generating potential of a silicate melt is promoted by the interaction of silicates having various composition and formed at different depths. This situation can arise during both the ascent of a mantle melt and the descent of crustal blocks in the mantle.

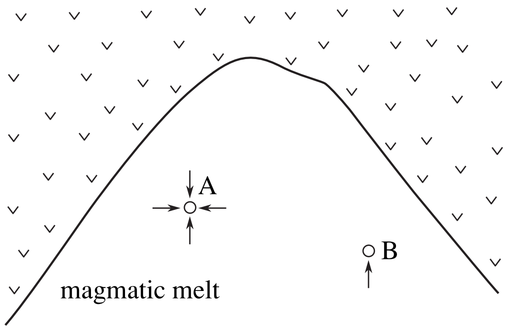

Fig. 2. Scheme of the effects of various factors on fluid inclusions in magmatic melt.

MECHANISMS OF THE FORMATION, OPERATION, AND EVOLUTION OF THE HYDROTHERMAL SUBSYSTEM

The mechanism of exsolution of a fluid phase from a melt is of great importance for the elucidation of relationships between magmatism and ore formation. As is widely known, the soft spot shared by several works devoted to this problem is the fact that “they do not consider the exsolution mechanism of volatiles and their migration from the melt into its host rocks” (Sharapov and Averkin, 1990, p. 36). It seems to be expedient to consider the escape mechanism of the fluid phase from an intrusive body and the migration of this phase into the host rocks. Figure 2 schematically represents an emplaced magmatic melt and fluid inclusions at points **A** and **B**. Fluid inclusions in the melt are under the influence of the pressure and Archimedean force. At any point of the melt, the pressures are equal in all directions, the forces affecting the fluid inclusions are equilibrated (point **A**), and the migration of fluid is impossible. The Archimedean force caused by differences in density between the melt and fluids is directed upward (point **B**), and fluid inclusions may migrate if this force overcome the resistance of the melt viscosity. However, even in this situation, the inclusion will move only within the melt and has no possibility to leave it.

The solidification of the melt and fracturing are followed by the release and migration of fluids. Since pressures in the fluid (lithostatic) and in the host rock fractures (atmospheric or hydrostatic) are different, the fluid phase may migrate from the intrusion into the host rocks, with the direction of this movement determined by the maximum pressure gradient, i.e., by normals to the contacts. A scheme of the formation and operation of the system is shown in Fig. 3. To consider the migration dynamics of a fluid phase during melt solidification, the intrusion was arbitrarily divided into several zones. Fluid will be exsolved from the outer zone in the form of numerous thin flows over the entire intrusive

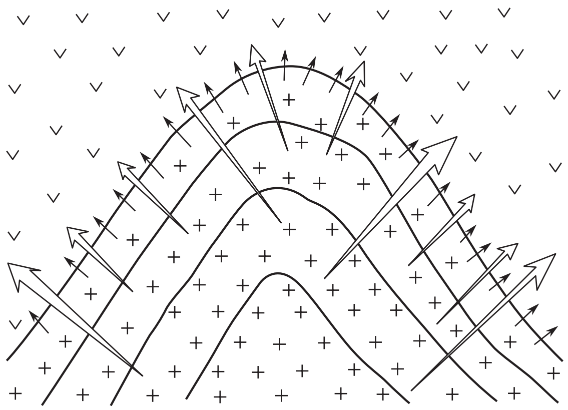

Fig. 3. Formation scheme of the hydrothermal system of the directionally moving solutions.

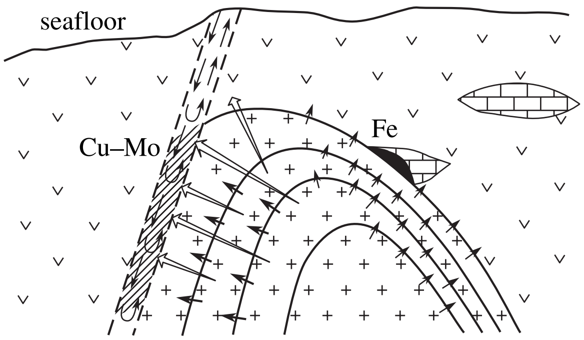

Fig. 4. Scheme of the paleogeological setting of the Tekhut Cu–Mo and Kokhb Fe deposits.

surface. Fluids from the inner zones are combined in progressively larger but fewer flows, because they are drained by thicker channels when passing through already-solidified and more fractured rocks. This is a general scheme of the formation of a hydrothermal system of directionally moving solutions. With increasing distance to the source and a pressure decrease, the ore-bearing solutions move with decreasing velocities and eventually stop, forming a convective–circulation hydrothermal system driven by the thermal energy of the intrusion.

The mechanism proposed for the development of a hydrothermal system implies some its features. In particular, the composition of the generated ore-bearing solutions remains unchanged throughout the period of their generation. Even if the composition of the fluid phase changes during the crystallization of the melt, the fluids would universally have the same composition when leaving the intrusion. This means that the precipitation of different mineral assemblages depends on a diversity of ore-controlling factors affecting the multicomponent solution rather than on the compositional variations in the ore-bearing solutions. Since the generation of the ore-bearing solutions begins when the near-contact zone of the intrusion is solidified and continues up to complete solidification of the inrtusion, the ore-bearing solutions are continuously supplied into the ore precipitation zones. Within the framework of this mechanism, the discontinuous character of ore precipitation observed at many deposits can be explained by the repeated reestablishment of the conduits of the hydrothermal solutions, which is caused, on the one hand, by formation mechanism of the hydrothermal system and, on the other, by changes in the fracturing style of the host rocks.

The aforesaid considerations based on the theoretical analysis of the formation and evolution of the hydrothermal system are confirmed by results obtained on the Kokhb–Shnokh ore–magmatic system. As was mentioned above, it consists of the Tekhut Cu–Mo porphyry deposits and the Kokhb and Miskhan contact–metasomatic Fe occurrences.

The Tekhut deposit is located in the western inner contact of the intrusion, being confined to the NE-trending fault zone with shattered rocks. The occurrences of Fe mineralization are situated in Late Jurassic volcanosedimentary rocks with lenses of marbleized limestones in the northeastern and southeastern outer contacts of the intrusion.

Filled with seawater, the fault zone served as a convective–circulation system, which removed heat and maintained the intense cooling of the intrusion on one side (Fig. 4). Evidently, the higher cooling rate, the thicker the solidified rocks, and the greater amount of ore-bearing fluids is generated in this direction.

This fact explains the differences in the scales between the Tekhut deposit, on the one hand, and the Kokhb and the Miskhan deposits, on the other hand. At the Fe occurrences, the mineralization is present in the form of dissemination and lens-pocket bodies, which is consistent with ore precipitation from flows of variable thickness. The definite relation of these occurrences to limestones points to the ore-controlling significance of the latter. The participation of the limestones in the ore formation is supported by isotope data and the composition of the precipitating minerals. The limestones have heavier oxygen and carbon isotope compositions than the ore-bearing solutions and serve as an oxidizer. They are more abundant at the Miskhan than at the Kokhb occurrence. Correspondingly, the ore-bearing solutions at the Miskhan occurrence have a 2.5‰ higher $\delta^{18}O$ value and 1.5‰ higher $\delta^{13}C$ than those of the Kokhb deposit, while the hematite–magnetite ores of the Miskhan occurrence have a higher hematite content (25% as compared to 18%). The correlation between the degree of Fe oxidation and the amount of oxidizer witnesses the in situ formation of the Fe ores.

The considered petrogenetic mechanism of the intrusion formation suggests that the ore-bearing solutions were enriched in Fe and depleted in S. Actually, pyrite accounts for more than 90% of the ore minerals at the Tekhut deposit, while the amount of S-bearing

Table 2. Oxygen isotope composition of quartz, calculated values of $\delta^{18}O$ of water and rocks at the Kadzharan deposit, homogenization temperatures of gas–liquid inclusions in quartz

Sample no.	Mineralization stages	$\delta^{18}O$, ‰ (SMOW)			T, °C	Sample group
		Quartz	Water	Rock		
4/85	Quartz–magnetite	10.2	8.1	8.9	520	I
2/85	Quartz–feldspar	10.0	7.1	8.3	460	
24/70	Quartz–molybdenite	10.1	6.7	8.6	430	
1/75	Quartz–molybdenite	9.7	6.1	8.1	420	
14/70	Quartz–molybdenite	9.6	6.0	8.0	420	II
32/70	Quartz–molybdenite	9.8	5.7	8.1	400	
23/70	Quartz–molybdenite	9.8	5.7	8.1	400	
25/70	Quartz–molybdenite	9.7	5.6	8.0	400	
12/64	Quartz–molybdenite	9.7	5.6	8.0	400	
33/70	Quartz–molybdenite–chalcopyrite	9.6	5.0	7.9	375	
244	Quartz–molybdenite	9.8	5.0	8.0	370	
28/70	Quartz–chalcopyrite	9.9	5.1	8.0	370	
30/70	Quartz–molybdenite	9.9	4.6	8.0	350	
74/k	Quartz–molybdenite–chalcopyrite	10.1	4.2	8.0	330	
77/k	Quartz–chalcopyrite	10.2	3.9	8.1	315	
17/63	Quartz–sphalerite–galena	7.3	0	4.9	290	III
13/65	Quartz–pyrite	8.1	–0.4	5.5	260	
39/70	Quartz–pyrite	7.5	–0.6	5.3	260	
3/70	Quartz–sphalerite–galena	6.7	–2.3	4.0	250	
4/70	Quartz–pyrite	7.0	–2.7	4.7	235	

minerals correlates with faulting, thus suggesting an external source of sulfur. In particular, the Miskhan and Kokhb contact–metasomatic Fe deposits contain ~3% sulfides (late-stage) and are devoid of sulfates. The Bover quartz–hematite vein deposit contains no more than 9% sulfides, while the Tekhut Cu–Mo deposit contains up to 95% sulfides and widespread sulfates. Sulfur could be derived from seawater. The oxygen (2.8–5.0‰) and hydrogen (from –40 to –20‰) isotope compositions of the ore-forming solutions point to mixing between seawater and magmatic solutions. At the same time, the sulfur isotope composition of sulfates of the Tekhut deposit ($\delta^{34}S$ = 16.6‰) corresponds to that of the Jurassic–Cretaceous sea, while the precipitation temperature of the sulfide assemblages (300°C and more) corresponds to the temperatures of abiogenic sulfur reduction in marine sulfate.

The operation of hydrothermal subsystems and their change define features of these subsystems and the spatial distribution of various mineral assemblages. This can be illustrated by the Kadzharan ore–magmatic system, including the Vokhchi multiple granite–granodiroite complex, the giant Kadzharan Cu–Mo porphyry deposit, and numerous diverse occurrences. The ore–magmatic systems formed after the collision, in a complex geodynamic setting of alternating extensional and compressional events.

The deposit is made up of an intrusive complex of variable age of the large (>1000 km^2) Megri pluton and a widespread series of diverse granodiorite dikes and stock-shaped bodies. The host rocks belong to the monzonite complex (37–38 Ma), while the ore-bearing rocks affiliate with the granite–granodiroite complex (22–24 Ma). These rocks are in tectonic contact through the deep-seated Tashtun fault. The ten mineralization stages recognized there are as follows: quartz–magnetite, quartz–feldspar, quartz–molybdenite, quartz–molybdenite–chalcopyrite, quartz–chalcopyrite, quartz–pyrite, quartz–sphalerite–galena, carbonate, chalcedony, and anhydrite–gypsum (Karamyan and Faramzyan, 1960). The temperature distinctly decreases from early to late stages. The mineral assemblages show horizontal zoning with respect to the granite–granodiorite intrusion.

Table 2 demonstrates the $\delta^{18}O$ and precipitation temperature of quartz from different assemblages, which were used to calculate the $\delta^{18}O$ of the water in the ore-bearing solutions. Samples are arranged in the table in order of decreasing temperature. The variations in isotope composition will be considered in the same succession, though the aforesaid succession of mineral

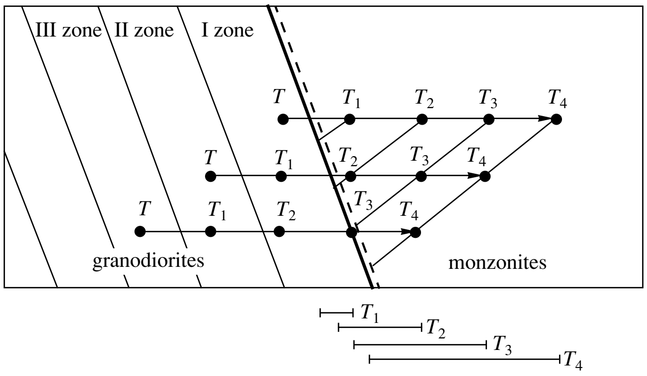

Fig. 5. Formation scheme of the horizontal zoning of the Kadzharan deposit.

precipitation was sometimes disturbed. The values of δ^{18}O of quartz and water correlate with the temperature, whereas the compositions of mineral assemblages show no correlation with the temperature, and the temperature ranges of adjacent assemblages overlap. From early to late assemblages, δ^{18}O in the solutions decreases, presumably owing to interaction between solutions and host rocks and mixing between surface waters and magmatic solutions. It is highly impossible to distinguish between these processes based only on the δ^{18}O of water, and the calculated δ^{18}O of the rocks are required. The value of δ^{18}O of plagioclase calculated from the plagioclase–water equation (O'Neil and Taylor, 1967) was taken as the approximate oxygen isotope composition of the rock. No high accuracy is necessary in this case, since these data are required to compare the variations in observed and calculated δ^{18}O values.

Ore precipitation at the Kadzharan deposit begins with the quartz–magnetite assemblage at a temperature of 520°C and δ^{18}O of the ore-bearing solutions of 8.1‰. Based on the subsolidus temperature of the solution, these values can be considered to be initial. The approximate oxygen isotope composition of the sources of these solutions is 8.9‰. The oxygen isotope compositions of monzonites and granodiorites are, respectively, 6.5–8.6 and 8.7–9.0‰, i.e., the ore-bearing solutions were derived from the Vokhchi granite–granodiorite intrusion rather than from the monzonite complex. The inferred structure of the deposit with this assumed source is shown in Fig. 5. The source of the solutions is subdivided into discrete zones to consider the evolution of the deposit during solidification (left-hand side of the figure), while the ore-hosting monzonites are shown in the right-hand side. Arrows indicate the movement of solutions from the corresponding zones into the monzonites. After the crystallization of zone I and fracturing, ore-bearing solutions are released at temperature T and migrate into monzonites. With increasing distance from the source, the temperature and pressure of the solutions decrease, and their interaction with the rocks causes compositional changes. The solutions of zone I have different temperatures at different distance from the source, T_1, T_2, T_3, and T_4 under conditions $T > T_1 > T_2 > T_3 > T_4$. Since certain temperatures correspond to certain mineral assemblages, different mineral assemblages are simultaneously deposited at different distance from the source or in different parts of the deposit. The cooling of the intrusion leads to the crystallization of subsequent zones, displacement of the regions of the solution generation inward the intrusion, and the shift of the precipitation sites of the corresponding mineral assemblage closer to the intrusion. Since mineral assemblages replace one another at definite sites of the deposit, the same assemblages are precipitated at different sites and at different times.

The precipitation sites of the same assemblages in Fig. 5 are connected by inclined lines, while their horizontal projections show the inferred abundance of the corresponding assemblages. The highest temperature assemblage is located closer to the source and is spread least widely, while later assemblages show increasing abundance and are located at an increasing distance from the intrusion, thus forming a zoned pattern. This tendency can be seen in the spatial distribution of quartz–magnetite, quartz–feldspar, quartz–molybdenite, and quartz–chalcopyrite assemblages at the Kadzharan deposit. The quartz–molybdenite and quartz–chalcopyrite assemblages are typically separated by the quartz–molybdenite–chalcopyrite assemblage, which also composes a zone but is less abundant than the previous one. The composition of the intermediate assemblage indicates that it was formed by the superposition of quartz–chalcopyrite assemblage onto quart–molybdenite one. Isotope data confirm this conclusion. The samples are subdivided into three groups according to their calculated δ^{18}O values (Table 2). The supply of the ore-bearing solutions into monzonites produced a disequilibrium system, whose tendency to equilibrium results in a lighter oxygen isotope composition of water and a heavier oxygen isotope composition of the monzonites. However, while information on the solution source is retained, the calculated δ^{18}O values of the rocks follow the variations in the δ^{18}O of water (group I of samples). After the recovery of equilibrium (Sample 1/75), this tendency would be changed. The second group of samples shows a decrease in the δ^{18}O of water at a nearly constant δ^{18}O of the rock (~8‰), which indicates the lightening of the oxygen isotope composition of the system owing to the influx of water with isotopically light oxygen. These samples preserve a near-equilibrium state caused by the compensation of the isotope effects of the temperature decrease and the influx of isotopically light water. The samples of group III show a sharp (~4‰) decrease in δ^{18}O of water to –2.7‰ and below –3.7‰ during the carbonate stage, indicating a meteoric origin of the water and transition to a convective–circulation hydrothermal system.

Ore deposition from the system of directionally moving solutions is related to the interaction of the solutions with host rocks or with the material filling fractures in these rocks (air, water, and others). The deposition of the quartz–magnetite assemblage is caused by interaction between the solutions and atmospheric oxygen. The solutions filling fractures in monzonites gradually replace air and stop precipitating this assemblage. The quartz–feldspar stage was marked by the pervasive alteration of monzonites instead of the deposition of ore minerals. This leads us to the conclusion that the solutions experienced significant changes, and this stage was preparatory for molybdenite precipitation. Since the quartz–molybdenite assemblage precipitated under nearly equilibrium conditions, the wallrock alterations are insignificant in spite of the high intensity of this ore stage. The deposition occurred under reducing conditions induced by interaction between solutions and monzonites. With increasing contribution of meteoric water with atmospheric oxygen, the reducing conditions give way to oxidizing ones, and the quartz–molybdenite assemblage is replaced by the quartz–chalcopyrite one. Given that molybdenite and chalcopyrite precipitated under reducing and oxidizing conditions, respectively, the formation of the independent quartz–molybdenite–chalcopyrite assemblage seems to be highly improbable.

A change in the hydrothermal system type is accompanied not only by a sharp decrease in $\delta^{18}O$ of solution waters, but also by a change in the ore composition, because the type of the hydrothermal system controls ore deposition. The individual sites of convective–circulation system differ in physicochemical conditions, allowing the formation of diverse minerals. Unlike hydrothermal system of directionally moving solutions, this system enables the mixing of the solutions and the simultaneous deposition of minerals formed under different physicochemical conditions. During this case, the mineral composition of the ores is determined by the law of mass action rather than by ore-controlling factors. The earliest assemblage contains minerals of the element, which is the most abundant in the solution and shows the largest abundance at the deposit. With decreasing content of the metal, the subsequent assemblages are formed by minerals of less abundant metals, the composition of the ore changes, and the subsequent minerals assemblages are characterized by a much lower abundance than the previous ones. As a result, the ore mineral assemblages are replaced by barren ones. Naturally, with the cooling of the intrusion and the solidification of the melt, the convective–circulation system is displaced toward the intrusion, and the subsequent mineral assemblages are shifted in the same direction. At the Kadzharan deposit, the quartz–pyrite assemblage is the most removed from the ore-bearing intrusion, while the latest anhydrite–gypsum assemblage is located immediately near the intrusion. Thus, the structure of the Kadzharan deposit is consistent with the derivation of the ore-bearing solutions from the Vokhchi multiple granite–granodiorite complex. Moreover, the tendencies in the ore distribution relative to the source of the hydrothermal solutions rule out the possibility of alternative sources, for example, the fairly popular "deep-seated source" of hydrothermal solutions. If mineralization is related to a deep-seated source, the aforementioned relations should be observed with respect to this source. If the solutions move horizontally, the source and deposit must be located at approximately equal depths (for example, the Vokhchi intrusion and the Kadzharan deposit). The vertical migration of solutions is responsible for the vertical zoning, while the source can be located somewhat deeper than the deposit. An amagmatic source of the solutions is ruled out, because these solutions could not produce a hydrothermal system of the solutions that moved directly away from the intrusion into the host rocks.

As was mentioned above, the contribution of meteoric water to ore formation is made possible by a decrease in the pressure of the magmatic solutions and attains a maximum in the convection–circulation system.

It should be noted that even isotope study can lead to erroneous conclusions without definite concepts on the evolution of the hydrothermal system. The following conclusions can be drawn from the isotope study of the Kadzharan deposit for the vertical migration of the ore-bearing solutions in the supra-intrusion zone. First, the quartz–pyrite assemblage precipitating from the convective–circulation system seems to be the most distant from the intrusion. Correspondingly, this assemblage, and possibly, also the quartz–sphalerite–galena and carbonate assemblages were first to be exposed by erosion. In this case, the researcher can obtain data only on these three assemblages with negative oxygen isotope composition of water. This will inevitably lead to the erroneous conclusion that the ore-bearing solutions were amagmatic in origin, inasmuch as neither the intrusion nor the early high-temperature assemblages are exposed.

CONCLUSIONS

1. The decisive factor determining the ore potential of the multiple gabbro–granite complex is its origin by means of the assimilation of acid crustal material by the parental mantle melt.

2. The ore fluids were obtained from certain intrusive complexes. The generation of ore-bearing fluids was simultaneous with the solidification of the melt and terminated upon the completion of this process. This process was accompanied by the formation of hydrothermal systems of directionally moving solutions, which gave way to a convective–circulation system. It should be noted that ore-generating hydrothermal system was not continuous but consisted of discrete flows

of directionally moving and convective–circulation hydrothermal solutions.

3. During the development of the deposit, the spatial position of the directionally moving and convective–circulation solutions changes, causing the supply of the ore-bearing solutions to different sites. This predetermined the pattern of the intermittent ore precipitation observed at the deposits, though solutions were uninterruptedly supplied to the deposit.

4. The stages of ore deposition do not correspond to certain time intervals in the evolution of the deposit, which is characterized by definite composition of ore-bearing solutions, but rather to the actual physicochemical state of the solutions, which is attained owing to interaction with the environment. As a result, various mineral assemblages simultaneously precipitated at different sites of the deposit and similar assemblages could be precipitated at different time.

5. The formation of the deposits of diverse metals, which are related to the same intrusive complex, or a change in mineral assemblages are caused by the influence of various geochemical barriers rather than by compositional variations in the hydrothermal solutions.

6. The ore deposition in the hydrothermal system of directionally moving solutions is determined by certain ore-controlling factors. A change in mineral assemblages is caused by a change in the redox conditions, and the earliest, highest temperature assemblage is located most closely to the source and is the least abundant. The subsequent lower temperature assemblages are more abundant and are located at increasing distance from the solution source. This results in formation of zoning along the direction of solution movement.

7. In the convective–circulation system, ore-controlling factors show no effect on the ore precipitation. Since this system is characterized by different physicochemical conditions at various branches and levels, it could completely release useful components. However, according to the law of mass action, the compositions of mineral assemblages are defined by the ore minerals of the predominant metals. Unlike the hydrothermal system of directionally moving solutions, the earliest assemblage in this system is the most abundant and the most distal from source. In other words, zoning in a hydrothermal system of directionally moving solutions develops away from the intrusion, while that in the convective–circulation system develops toward the intrusion.

This study was financially supported by the Republic of Armenia.

REFERENCES

1. M. S. Akopyan and R. L. Melkonyan, “Isotope–Oxygen Indicators of Differentiation and Assimilation,” in *Oceanic Magmatism. Evolution, Geological Correlation* (Nauka, Moscow, 1986), pp. 133–138 [in Russian].
2. M. S. Akopyan and R. L. Melkonyan, “Petrology of the Intrusive Complexes of the Alaverdy Ore District Based on the Isotope–Oxygen Data,” Geokhimiya, No. 6, 850–863 (1981).
3. A. T. Aslanyan, M. S. Akopyan, R. L. Melkonyan, and V. O. Paronikyan, “Kokhb–Shnokh Paleoisland-Arc Ore Magamtic System and a Model of Its Formation,” Geokhimiya, No. 1, 91–105 (1990).
4. K. A. Karamyan and A. S. Faramazyan, “Mineralization Stages of the Kadzharan Copper–Molybdenum Deposit,” Izv. AN ArmSSR. Geol. Geograf. Nauki, Nos. 3–4, 65–88 (1960).
5. C. E. Hedge, “Strontium Isotopes in Economic Geology,” in *Stable Isotopes As Applied to Problems of Ore Deposits* (Econ. Geol. **69**, 1974; Mir, Moscow, 1977), pp. 823–825.
6. B. M. Meliksetyan and R. L. Melkonyan, *Petrology and Geochemistry of Intrusive Complexes of Some Ore Districts of Armenian SSR* (Akad. Nauk Arm. SSR, Yerevan, 1976) [in Russian].
7. R. L. Melkonyan and R. Kh. Gukasyan, “Problems of the Age of the Kokhb–Shnokh Intrusive Complex,” Izv. NAN Respubl. Armeniya. Nauki o Zemle, No. 1, 29–35 (2004).
8. J. R. O’ Neil and H. P. Taylor, “The Oxygen Isotope and Cation Exchange Chemistry of Feldspars,” Am. Mineral. **52**, 1414–1431 (1967).
9. Yu. D. Pushkarev, “Two Interaction Modes of Crustal and Mantle Materials and a New Approach to Problems of Deep Ore Formation,” Dokl. Akad. Nauk **355** (4), 524–526 (1997) [Dokl. Earth Sci. **355** (6A), 881 (1997)].
10. V. N. Sharapov and Yu. A. Averkin, *Dynamics of Heat- and Mass-Transfer in the Orthomagmatic Fluid Systems* (Nauka, Novosibirsk, 1990) [in Russian].