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SHORT COMMUNICATIONS

Rb–Sr Dating of Gold–Sulfide Mineralization in the Shaukhokh Orefield, North Ossetia, Russia

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INTRODUCTION

Isotopic dating of metasomatic ore mineralization is often a challenging problem, particularly if this mineralization is hosted in carbonate rocks. The low K, Rb, and REE concentrations preclude the application of K–Ar, Rb–Sr and/or Sm–Nd techniques in their classic modifications. Moreover, the latter technique is practically never applicable to young Meso-Cenozoic rocks, at which our study was centered. The absence of syngenetic U-bearing phases, such as zircon, also precludes the use of U–Pb dating techniques.

In studying disseminated gold mineralization at the Shaukhokh orefield in North Ossetia, we faced the problem of possible genetic relations between the Au–Ag ore mineralization and endogenic processes, namely, Jurassic and Neogene magmatism [1]. This issue could obviously be elucidated via dating the hydrothermal–metasomatic process that produced the Au–Ag mineralization.

We attempted to resolve this problem by applying unconventional approach to the Rb–Sr dating of metasomatized rocks, which are dominated by carbonate material and contain fairly much Sr (350–1100 ppm) and very little Rb (4–9 ppm).

GEOLOGICAL OVERVIEW

The Shaukhokh orefield is localized in the Adaikhokh–Shaukhokh–Darial tectono-stratigraphic zone in North Ossetia, in the upper reaches of the Midagrabidon River, at elevations of 2000–2400 m a.s.l. Sevosgeologorazvedka has discovered gold mineralization at the Kabutau and Lartsodon prospects in the form of gold–sulfide–carbonaceous associations. The ore mineralization is hosted by rocks of the carbonaceous–terrigenous association: conglomerates and gritstones of the Badskaya Formation (Late Carboniferous), metasands and shales of the Midagrabinskaya Formation (Late Carboniferous–Early Permian), marmorized limestones with carbonaceous matter and marbles of the Gizeldonskaya formation (Early–Middle Permian), and quartzite–sandstone of the Kistinskaya Formation (Early Jurassic). The rocks are locally biotitized, cut by zones of metasomatic alterations (with quartz, epidote, sericite, actinolite, and chlorite), often contain fine disseminated sulfides in the form of abundant pyrite metacrysts, pockets, and veinlets, and also often bear disseminated fine pyrrhotite. Exploration at the Shaukhokh orefield made it possible to outline economic mineralization and evaluate its predicted gold resources (category P2) at 9.4 tons at a cutoff grade of 0.9 g/ton [2]. It would be of much economic importance to elucidate the possible genetic relations between the ore mineralization of the type with any of the magmatic rocks of various age found in the area. The Shaukhokh orefield and its surroundings are known to host rocks of the dike suite of the diabase–picrite association (Middle Jurassic), subvolcanic facies of the Lartsokomskii stock (andesidacites and other rocks provisionally dated at the Middle Neogene), and numerous exposures of rocks of the Dzhimarskii polyphase granitoid massif of Pliocene age [1].

METHODS

Our Rb–Sr isotopic studies were carried out at the Laboratory of Isotopic Chemistry and Geochronology of the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. The Rb and Sr concentrations were measured by isotopic dilution techniques. The samples (20–30 ng) were spiked with a mixed ^{84}Sr–^{85}Rb tracer and then dissolved in HF + HNO_3 mixture in the proportion 5 : 1. The material was decomposed for 3 days in Teflon

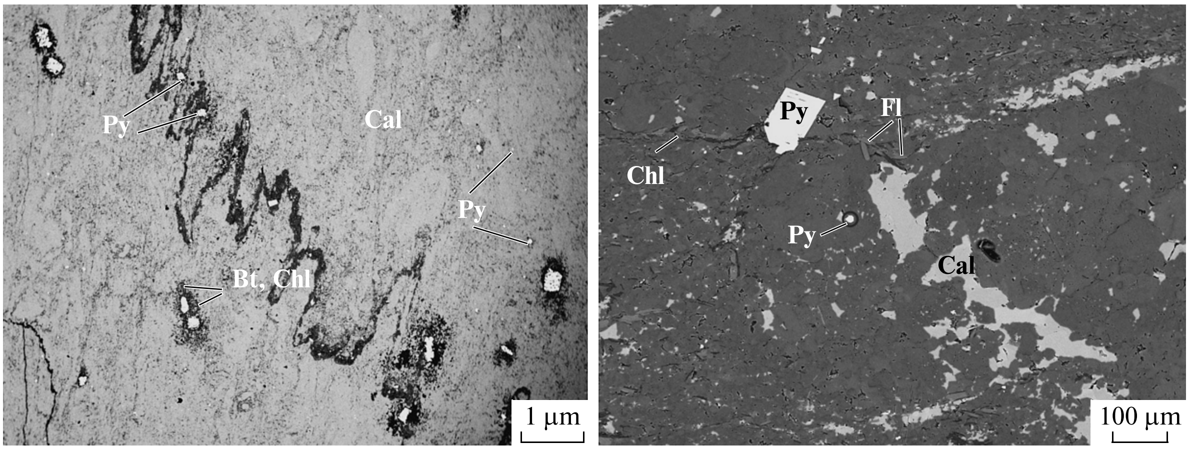

Fig. 1. Distribution of minerals in samples SU-9 (left) and SU-10 (right). The electron images are recorded in back-scattered electrons at an accelerating voltage of 20 kV and current close to 2 nA.

weighing bottles under a lamp at continuous stirring. The dry residue was then transformed into chloride via triple evaporation in concentrated HCl, after which Rb and Sr were extracted by chromatographic techniques. The Sr isotopic composition and the Rb and Sr concentrations were measured on Triton multicollector mass spectrometer. The analysis of the SRM-987 Sr standard during this study yielded 0.710245 ± 11 ($2\sigma_{ave}$, $N = 13$), which corresponds to a relative error of an individual analysis of 0.006% for the $^{87}Sr/^{86}Sr$ ratio. The relative error of the $^{87}Rb/^{86}Sr$ ratio is 1%. These error values were utilized in calculating the isochron parameters with the Isoplot 3.0/Ex program package [3]. The parameters of the parallel isochrons were calculated by the method [4].

The composition of our samples was examined at the Laboratory of High Spatial Resolution Analysis at the Geological Faculty of the Moscow State University on a Jeol JSM-6480LV electron microscope with a W thermoemission cathode, equipped with an INCA-Energy 350 energy-dispersive spectrometer with a Li–Si semiconductor detector 10 mm^2 in area and a superthin ATW-2 slit (resolution 129 eV at Kα Mn).

The X-ray powder diffraction studies were conducted on a DRON-UM1 at the Geological Faculty of the Moscow State University.

MINERALOGY OF THE SAMPLES AND THEIR PREPARATION FOR ANALYSIS

Our geochronologic study was carried out with two samples selected from our collection: SU-9 and SU-10 from the Lartsidon prospect on the right-hand bank of the Midagrabidon River. Sample SU-9 was taken at the headwaters of Fidarkom Stream at an elevation of 2400 m a.s.l. Sample SU-10 was taken at a distance of 400 m from SU-9, in the right-hand bank of the same stream, at an elevation of 2120 m a.s.l. As can be seen in thin sections under a microscope, both rocks are dark gray massive marmorized carbonate rocks with pronounced schistosity. They are cut by veinlets of various thickness, from a few fractions of a millimeter to 1 cm. The rocks are medium-grained blastomylonitic, with lens-shaped calcite lithoclasts ranging from 1 mm to 1 cm, which are surrounded by a schistose fine-grained lepidogranoblastic matrix. The matrix of sample SU-9 consists of calcite and dolomite, and that in SU-10 is composed of calcite. The finely divided disseminated carbonaceous matter is included in grains or is locally concentrated along their boundaries, and its content can reach 10%. The rocks contain silicate minerals in the form of veinlets, often in sheared zones.

Sample SU-9 contains carbonate veinlets of two structural types: those with linear smooth boundaries and branching veinlets of variable thickness, which contained extensively oxidized pyrite grains. The veins show traces of carbonate recrystallization. Ore minerals occur throughout the whole volumes of samples SU-9 and SU-10 (Fig. 1): they are contained in the carbonate matrix, in veinlets, and in sheared domains. The grains of the ore minerals range from 20 to 100 μm and compose two populations: (i) an older one, which was related to the sedimentation process (sulfides that were contained in the sedimentary rock and gave rise to the older pyrite when recrystallized) and (ii) that corresponding to the deposition of newly formed ore material (thereby older sulfide grains retained their morphologies and served as seed crystals).

The protolith of the marmorized carbonaceous limestone and marble of the Gizeldon Formation consisted of sedimentary carbonate material with minor admixtures of aluminosilicate material, which gave rise to chlorite, sericite, and biotite after recrystallization. Recrystallization resulted in the coarsening of

Rb–Sr isotopic and X-ray powder diffraction data

Sample	Fraction	Mineralogical composition	Rb, ppm	Sr, ppm	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr
SU-9m	Magnetic	Dol*, Ank, Bt, Clc	61.6	73.2	2.438	0.714775 ± 13
SU-9nm	Unmagnetic	Ank, Clc, Ms	35.1	49.2	2.061	0.713880 ± 9
SU-9 WR	Pristine rock	Dol, Cal, Clc	8.88	346.3	0.0742	0.709492 ± 15
SU-10m	Magnetic	Ms, Clc	37.2	63.5	1.695	0.711394 ± 12
SU-10nm	Unmagnetic	Clc, Cal, Ms	59.2	116.8	1.466	0.710804 ± 10
SU-10 WR	Pristine rock	Cal, Ms, Clc	4.01	1126	0.01031	0.707537 ± 6

* Dolædolomite, Ankæankerite, Btæbiotite, Clcæclinochlore, Msæmuscovite, Calæcalcite.

mineral grains and their purification, and the silicate material was thereby segregated. The process of recrystallization occurred in two pulses. The first of them took ploace during late catagenesis and involved the recrystallization of calcite and the development of veinlets [5]. The younger episode was related to the overprinted hydrothermal process and involved the recrystallization of the silicate material and the deposition of the gold–sulfide ore mineralization. Silicates contained in the rocks in the form of cutting veinlets to which ore minerals and biotite are spatially restricted. The hydrothermal process, which was likely driven by the emplacement of intrusions, overprinted the already-recrystallized carbonate matrix. The temperature of the hydrothermal processes was evaluated based on the composition of the chlorite at 260–320°C [6, 7].

Electron microscopic and microprobe data indicate that sample SU-9 contains biotite, chlorite, albite, sphene, pyrite, and minor amounts of galena. Sample SU-10 contains biotite (which is locally chloritized), albite, quartz, apatite, and ore minerals (pyrite, pyrrhotite, galena, and Ag telluride). Other samples from the Lartsidon Prospect were determined to contain, along with the aforementioned minerals, also U and Th silicates, epidote, cobaltite, and muscovite.

Isochrons are traditionally constructed based either on a group of whole-rock samples or on monomineralic fractions separated from a single rock sample. These approaches are, however, inapplicable to dating hydrothermal–metasomatic rocks. An unconventional approach to Rb–Sr dating mineralized veins and metasomatites was suggested in [8, 9]. This approach involves the technique of monomineralic isochrons, in which the isochrons are based on data on a number of fractions of the same mineral [8] or on fractions of different density obtained from a single sample [9]. The approach sometimes makes it possible to distinguish between mineral grains affected and not affected by secondary processes.

However, we failed to successfully apply any of these approaches in dating rocks from the Shaukhokh orefield. First of all, we rejected Rb–Sr dating of whole-rock samples because the groundmass of the rocks is made up of carbonates, in which the content of the radiogenic component approaches zero because of the extremely low Rb/Sr ratio. The size of the aluminosilicate grains suitable for dating was too small (approximately 20–70 μm) to separate them as individual fractions. Because of this, we decided to chemically get rid of the carbonate constituent of the rocks and thus leave only the silicate minerals appropriate for Rb–Sr dating. For this purpose, we placed small rock fragments into a 50-ml test tube, poured 15% acetic acid into it, capped tube, and left for 2 days. Acetic acid (but not, for example, chlorhydric acid) was used because strong acids could perturb the structures of the silicates and partly leach Rb and/or Sr from them, whereas weak acids were able to dissolve only the carbonate material and could not damage the silicate minerals. The silicate fraction that was not dissolved in the acid was filtered, dried, and subdivided into two fractions: magnetic and nonmagnetic. Eventually, we obtained three fractions from each of the samples: pristine rock and its magnetic and nonmagnetic fractions. Our X-ray powder diffraction data indicated that all of the fractions of both samples contained carbonates (dolomite, calcite, and ankerite), Mg–Fe chlorite, biotite, and muscovite in variable proportions. The grains of the ore minerals (sulfides) were too small, they were contained in the rocks as disseminated phases, and none of them was identified by X-ray powder diffraction. The sulfides were completely dissolved during the further decomposition of the samples in acids.

RESULTS AND DISCUSSION

Our Rb–Sr isotopic data are summarized in the table and graphically represented in Fig. 2a, which displays the ^{87}Sr/^{86}Sr– ^{87}Rb/^{86}Sr dependences of both rocks. The data points of the two samples define two

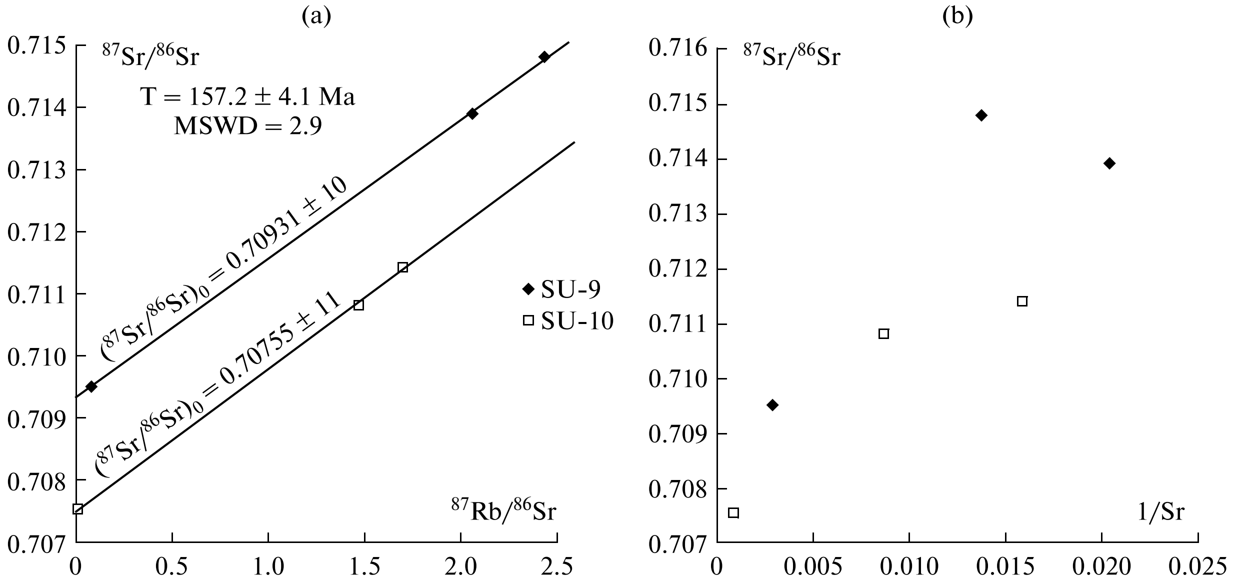

Fig. 2. (a) Rb–Sr diagram and (b) dependence of the Sr isotopic ratios on the Sr reciprocal concentration for samples SU-9 and SU-10 of carbonaceous marmorized limestone of the Gizeldonskaya Formation with gold–sulfide mineralization. The age and Sr initial isotopic ratios are calculated by the technique of parallel isochrons [4].

practically parallel isochrons that correspond to ages of 156.4 ± 1.9 Ma for sample SU-9 and 159.7 ± 2.5 Ma for sample SU-10, with remarkably different initial Sr isotopic ratios of 0.70932 ± 4 and 0.70751 ± 4, respectively. The statistical processing of the data with the parallel isochron technique [4] shows that the lines can be considered parallel with a probability of 95%, and their common age value is 157.2 ± 4.1 Ma at Sr initial isotopic ratios of 0.70931 ± 10 and 0.70755 ± 11.

In the course of metasomatism, Sr in the marmorized limestone could mix with Sr in the fluid. Then a mixing line could be drawn in the isochron diagram, with this line resembling an isochron but having no geochronologic sense. In order to test this hypothesis, we constructed a plot (Fig. 2b) for the dependence of $^{87}Sr/^{86}Sr$ and reciprocal Sr concentration. If the differences in the Sr isotopic composition are caused by two-component mixing, they should also exhibit dependences whose quality is no worse than that of the isochrons. In fact, the data points do define a certain trend (Fig. 2b) but never clkear-cut linear dependences, and the scatter of the points is much greater than for the isochrons in Fig. 2a. Hence, the derived dependences of $^{87}Sr/^{86}Sr$ on $^{87}Rb/^{86}Sr$ for both samples should correspond to isochrons but not lines of two-component mixing.

The initial isotopic ratios of the rocks turned out to be different, likely because of the isotopic heterogeneity of the host rocks. The isochrons obtained for the two samples provide sound grounds to believe that isotopic equilibrium was reached between all minerals in both of the samples in the course of metasomatism. The Sr isotopic composition was thus locally equilibrated on a scale of a hand specimen, whereas the host rocks as a whole remained isotopically heterogeneous. It is thus reasonable to believe that our dating strategy was a success.

When hydrothermal ore-forming processes took place immediately after the magmatic process, metasomatism proceeded in rocks whose Sr isotopic composition was still not heterogenized. In this situation, the dating can well be conducted on whole-rock samples, as was done, for example, in [10].

The similar ages of the two samples led us to believe that the soft leaching of carbonates resulted in the complete dissolution of the carbonate material without Rb fractionation relative to Sr, and hence, the Rb–Sr system reflects the time when isotopic equilibrium was reached between the carbonate and silicate constituents of the rocks, i.e., the time when the disseminated ore mineralization was deposited.

It follows that gold ore mineralization was produced in rocks of the Shaukhokh orefield in Jurassic time, likely in relation to the dike suite that belongs to the Kazbek subvolcanic–hypabyssal diabase–picrite association. Dikes of the complexes are traced as a discontinuous latitudinal stripe and consist of diabase, diabase porphyry, microgabbro, and other rocks. Geological relations indicate that the diabases of the Kazbek Complex were emplaced in post-Callovian time in the Middle Jurassic. Jurassic tectono-magmatic reactivation is typical of the Digoro–Ossetia tectono-stratigraphic megazone, which includes the Aidakhokh–Shaukhokh–Darial zone. Late evolutionary episodes of the emplacement of the Jurassic volcano-plutonic complexes were associated with the origin of base-metal deposits in the Sadon district and, as follows from our results, gold–sulfide ore mineralization in the Shaukhokh orefield.

CONCLUSIONS

The application of soft leaching allowed us to obtain Rb–Sr age of gold-bearing metasomatic mineralization in marmorized carbonaceous limestones at the Shaukhokh orefield. The parallel isochrons obtained for two samples correspond to an age of 157.2 ± 4.1 Ma (Sr initial isotopic ratios are 0.70931 ± 10 and 0.70755 ± 11), i.e., Middle Jurassic. Ore gold mineralization was thus produced at the Shaukhokh orefield in relation to the emplacement of the Jurassic dike suite of the diabase–picrite association.

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SPELL: 1. Neymark