

## Thermodynamic properties of minerals and fluids

Korepanov Ya.I., Osadchii E.G. Modeling of a gold-silver-tellurium phase diagram by experimental thermodynamic data of phases and solid solutions. UDC 550.4.02.

Institute of Experimental Mineralogy RAS

**Abstract** Based on the literature thermodynamic data for binary and ternary phases and our own data on the  $\text{Ag}_x\text{Au}_{1-x}$  solid solution, isothermal sections of the Ag-Au-Te phase diagram were calculated. The simulation was carried out using the TERNAPI program (Voskov et al, 2015). For the ternary associations (paragenesis) of  $\text{Ag}_2\text{Te}$ - $\text{Ag}_3\text{AuTe}_2$ - $\text{AgAu}$ , the compositions of the equilibrium alloy at temperatures of 323 and 373 K are given (table 2.). The temperature dependence of the composition of the alloy is about 2 at% Ag per 50 degrees.

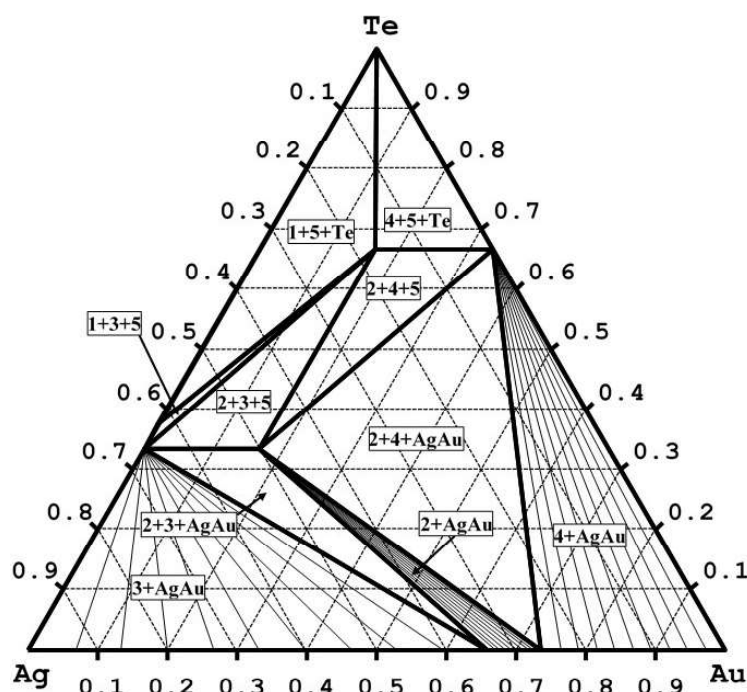
**Keywords:** Ag, Au, Te, alloy, thermodynamics, metals and solid solution, EMF.

**Introduction** Gold and silver tellurides do not have such importance as native gold, despite the fact that the Ag-Au-Te mineral associations (Fig. 1) are present in many gold deposits and the study of their thermodynamic properties is an important task for understanding the geochemistry, transfer processes and the formation of gold deposits.

Based on the published papers and data being prepared for printing on the Ag-Au-Te system, the possibility of a theoretical study of the phase diagram was obtained using TERNAPI (Voskov et al, 2015). To simulate the Ag-Au-Te phase diagram, the following data were used (Table 1):

**Table 1.** Thermodynamic data used for modeling.

Mineral	Composition	Equation	Temperature range	References
Empressite	$\text{AgTe}$	$-15980-14.88T$	282-465 K	Voronin et. al. 2017
Stutzite	$\text{Ag}_5\text{Te}_3$	$-110900+523.9T-86.55T \ln(T)$	298-672 K	
No mineral	$\text{Ag}_{1.9}\text{Te}_3$	$-34990+112.9T-21.21T \ln(T)$	386-667 K	
Hessite	$\alpha\text{-Ag}_2\text{Te}$	$-43620+175.9T-28.85T \ln(T)$	298-424 K	
	$\beta\text{-Ag}_2\text{Te}$	$-37330+146.1T-26.37T \ln(T)$	424-667 K	
Calaverite	$\text{AuTe}_2$	$-48094+439.5T-57.7T \ln(T)$	298-424 K	Echmaeva 2009
Petzite	$\text{Ag}_3\text{AuTe}_2$	$-56080 - 49.84T$	298-400 K	
Sylvanite	$\text{AuAgTe}_4$	$-98596+847.4T-115.4T \ln(T)$	298-424 K	
Ag-Au alloy	$\text{Ag}_x\text{Au}_{1-x}$	$-10^{-3} \cdot 96484.56 \cdot (590 \cdot x^2/3 + 350 \cdot x + 200 + 0.1806 \cdot T) \cdot x(1-x)$ (J/mol)	273-723 K	Preparing for publication



**Fig.1.** The ternary phase diagram of Ag-Au-Te, at a temperature 373 K, where 1 –  $\text{Ag}_5\text{Te}_3$ , 2 –  $\text{Ag}_3\text{AuTe}_2$ , 3 –  $\text{Ag}_2\text{Te}$ , 4 –  $\text{AuTe}_2$ , 5 –  $\text{AgAuTe}_4$ , 6 –  $(\text{Ag,Au})\text{Te}_2$ ,  $\text{AgAu}$  – solid solution  $\text{Ag}_x\text{Au}_{1-x}$

It was found that the ratio of silver and gold in the mineral association  $\text{Ag}_2\text{Te}$ - $\text{Ag}_3\text{AuTe}_2$ - $\text{AgAu}$  depends on the temperature of formation of parageneses. This fact can be used as a geothermometer.

**Table 2.** The composition of the alloy in field 2 (petzite) + 3 (hessite) +  $\text{Ag}_x\text{Au}_{1-x}$  (native gold)

Temperature	$\text{Ag}_2\text{Te}$ - $\text{Ag}_3\text{AuTe}_2$ - $\text{AgAu}$
323.15 K	$\text{Ag}_{0.329}\text{Au}_{0.671}$
373.15 K	$\text{Ag}_{0.343}\text{Au}_{0.657}$

Program Department of Earth Sciences RAS "Experimental study of mineral equilibria and isotopic ratios"

## References:

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## Makarov V.P. Experimental study of natural fractionation of argon isotopes. UDC: 550.42:550.93

Russian State Geological Prospecting University, Moscow.

**Abstract.** The field and experimental features of the isotope distributions in the triad ( $^{36}\text{Ar}$ ,  $^{39}\text{Ar}$ ,  $^{40}\text{Ar}$ ), mainly in biotite, at high T were analyzed. It was established that in pairs ( $^{40}\text{Ar}/^{36}\text{Ar}$ ) and ( $^{39}\text{Ar}/^{36}\text{Ar}$ ) a linear relationship is observed with and not related to the isochron. The  $^{40}\text{Ar}/^{39}\text{Ar}$ -T distribution is described by a parabolic equation, the total square of which has the form  $\ln(^{40}\text{Ar}/^{36}\text{Ar}) \approx -A(1/T - 1/T_0)^2 + B$ . Here  $RTA = \Delta H_0$  is the enthalpy of sublimation (dissolution), Ar isotopes, i.e. the heat of dissolution of the impurity (Ar) in the mineral at the temperature  $T_0$  (in Kelvin) of the mineral crystallization under natural conditions. They are related by the equation  $\Delta H_0 = 22.51T_0 - 10545$ .

**Keywords:** *sublimates, argon, temperature effects, parabolic equations, pressure of argon.*

The whole complex of geological observations on the behavior of the RGII (Radiogenic Isotopes and Isobar) in thermogradient fields indicates the possibility of fractioning them in natural conditions. The rare results of theoretical calculations available to us also speak of this possibility at high T. The purpose of the previously conducted experiments is to establish the degree of preservation of isotopic ratios under various thermodynamic conditions. At the same time, they have a number of common drawbacks: 1). They are not viewed from the position of isotope fractionation, but from the standpoint of the preservation of isotope ratios, which leads to ignoring the phenomenon of the equilibrium distribution of isotopes. 2). According to the theory of fractionation (TF), an analysis of the isotopic composition of the two compounds is necessary, but in experiments, as a rule, only one is studied. 3). All experimental studies ended with a qualitative statement of the results of changes in isotopic ratios without calculating the corresponding parameters: fractionation indicator, kinetic coefficients, etc.

Thus, if we rely on the theoretical and experimental materials on the fractionation of SILE (Stable Isotopes of Light Elements), then all experiments on the separation of the RGII were

performed methodologically at a low level. Below are the materials of the analysis of already conducted experiments on published data.

**Argon in natural formations.** These experiments are aimed at studying the features of migration and precipitation from the  $^{40}\text{Ar}$  crystal lattice under the influence of high T in order to identify the influence of metamorphism of rocks on the results of determining the age of these rocks by the K-Ar method. In Russian Federation on a large scale, these studies were conducted primarily by E.K. Gerling and H.I. Amirkhanov. However, from the point of view of analyzing the influence of T, these studies have significant drawbacks, the main ones of which are as follows:

1) according to the TF SILE, the effect of T on fractionation is not reflected by a change in the absolute contents of isotopes, but by a change in the ratios of these contents. This means that temperature analysis requires the ratio of two isotopes of at least one element. However, in the works mentioned above, only the  $^{40}\text{Ar}$  isotope was subjected to this analysis. True, recently, in connection with the advent of the age determination method by the  $^{40}\text{Ar}$  –  $^{39}\text{Ar}$  isotope ratio (Dalmeyr, 1984), the  $^{40}\text{Ar}/^{39}\text{Ar}$  ratio has been analyzed.

2) According to the theory of determining the age by the K-Ar method, the baseline for determining the age is the ratio  $^{40}\text{Ar}/^{40}\text{K}$ . However, in the presence of detailed studies on diffusion and loss of argon, there are practically no such studies for  $^{40}\text{K}$ . The available data suggests a possibility of migration of  $^{40}\text{K}$  at high T.

3) the inconsistency of the conditions of the experiments with Ar to the actual natural conditions and, therefore, the not completely correct interpretation of the phenomenon of "loss of argon" when heated. The fact is that when analyzing the temperature dependence of the amount of  $^{40}\text{Ar}$ , all experiments are conducted in vacuum or other gas (air, etc.) medium. But these are environments in which gaseous Ar is freely released and it was they that were taken into account when forming the hypothesis about the "loss" of Ar at heating (Amirkhanov, 1960). On the other hand, there are experimental data on the artificial introduction of Ar into minerals (Gerling et al., 1965) under conditions of increased Ar pressure. These experiments are usually not related to each other in any way. At the same time, in natural conditions minerals are, as a rule, in close intergrowth with each other, having numerous borders of contact. therefore, when heated, Ar must overcome precisely these boundaries and stand out primarily not into a vacuum, but into the surrounding minerals. Thus, the combination of both experiments leads to the conclusion about the usual isotopic exchange between two minerals, which was observed earlier in other isotopic systems.