

Evolution of the composition of hydrothermal mineral-forming fluid of ore deposits in early Precambrian of the Ukrainian Shield

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The aim of the study, the results of which are presented in this article, is to study changes in the composition of hydrothermal fluid ore systems of the early Precambrian on the example of gold and uranium ore deposits of the Ukrainian shield in connection with the evolution of exo- and endogenous processes in the outer shells of the Earth. The method used is a complex isotope-geochemical study of the composition of gas-liquid inclusions of hydrothermal fluid of ore systems. Based on experimental isotope-geochemical studies of the fluid of gas-liquid inclusions in the minerals of Precambrian deposits of uranium and gold of the Serednoprudniprovsky and Ingul megablocks of the Ukrainian Shield, a consistent change in the quantitative and isotopic composition of hydrothermal fluids of mineral formation from Mesoarchean to Paleoproterozoic was established. The content of H₂O and CO₂ was investigated and the isotopic composition of carbon CO₂ fluids in quartz, pyrite, and feldspar were studied. The age range of the studied deposits is 3200—1750 million years. A decrease in the carbon dioxide content in the hydrothermal mineral-forming fluid of the Precambrian occurred in the Neoproterozoic, that is, before the Great Oxygen Event (Great Oxidation Event) — an increase in the oxygen content in the atmosphere in the Paleoproterozoic and is probably associated with the processes of exogenous and endogenous hydration of ultramafic rocks during the formation of the protocontinental crust. Molar fraction of CO₂ in the mineral-forming fluid, in the Precambrian correlates to some extent with atmospheric pressure. The increase in the content of the carbon-12 isotope in the Paleoproterozoic in the mineral-forming fluid occurred due to the oxidation of organic matter with an increase in the oxygen content in the atmosphere.

Key words: Archean, Proterozoic, gold and uranium ore deposits, Ukrainian Shield, Serednoprudniprovsky and Ingul megablocks, protocontinental crust, hydrothermal fluid, isotopic composition.

Introduction. In the Archean, an important evolution of the interaction of the crust and mantle took place, which led to the emergence of the continental crust and continents [Som et al., 2012; Reimink et al., 2021], which in turn affected the oxygen isotopic composition of magmatogenic zircons [Valley et al., 2005]. There was also a change in the state of the fluid systems of magmatic melts from reducing to oxidizing [Letnikov, 1982].

The Archean-Proterozoic boundary is char-

acterized by a number of major changes in the Earth's evolution. Among them is a change in the atmosphere from oxygen-free to oxygen. This phenomenon Holland [Holland, 2002] gave the name «Great Oxygen Event». The appearance of oxygen in the atmosphere led to drastic changes in the Earth's outer shells [Lyons et al., 2014; Bekker, 2015].

Based on experimental isotope-geochemical studies of the fluid of gas-liquid inclusions (GLI) in minerals of different ages of uranium

and gold deposits in Ukraine, we found a significant difference in the isotopic composition of carbon and the molar fraction of CO_2 in the fluid of archean and proterozoic deposits [Belevtsev, Koval, 1995; Fomin et al., 2018], reflecting the phenomenon of evolution of hydrothermal fluids of mineral formation at the Archean-Proterozoic boundary.

Research methodology. A comprehensive isotope-geochemical study of the fluid in minerals included the isolation of GLI components, determination of the amount of water and CO_2 , isolated from inclusions, determination of the isotopic composition of oxygen and hydrogen of water and the isotopic composition of oxygen and carbon CO_2 . See the results of the study of the isotopic composition of oxygen and hydrogen [Fomin et al., 2018]. The separation of GLI components was carried out by mechanical crushing of 6 g of mineral monofraction in a vacuum mortar with preliminary degassing for 1 hour at a temperature of 393 K (120 °C) and a pressure of 4 Pa. After crushing, to eliminate the influence of sorption of components with mineral dust, the temperature was increased to 200 °C. Water and CO_2 , after separation, they were separated by distillation at a temperature of 198 K (–75 °C), CO_2 it was frozen in an ampoule, which was transferred for mass spectrometric measurement of the isotopic composition of carbon and the amount of CO_2 . The remaining water was frozen in an ampoule with zinc or guanidine hydrochloride to determine the isotopic composition of H or ^{18}O , respectively. The release of hydrogen from water was carried out by the reaction of its interaction with zinc at a temperature of 673 K (400°C) [Korostyshevsky et al., 1982]. Amount of water and CO_2 it was determined on a mass spectrometer simultaneously with the determination of the isotopic composition by the intensity of peaks of 2 amu and 44 amu, respectively, for which the mass spectrometer was calibrated by the content of water and CO_2 the molar fraction of CO_2 was calculated. Value $\delta^{13}\text{C}$ are given relative to the PDB (standard «Pee Dee Belemnite») from marine fossils of the Cretaceous Period *Belemnitella Americana* of the Pee Dee formation in South Carolina), the accuracy is $\pm 0.5\%$.

Research objects and their characteristics. Objects where the content of H_2O and CO_2 was examined and the isotopic composition of carbon CO_2 in GLI in quartz, pyrite and feldspar in the oligoclase system, orthoclase-microclin-albite belong to two regions (megablocks) of the Ukrainian Shield and simultaneously characterize three age groups — Mesoarchean, Neoproterozoic and Paleoproterozoic. Meso- and Neoproterozoic ages objects are represented by gold deposits of the Surska and Chertomlytsky structures of the Serednoprivodniprovska granite-green stone region (Sergiivske, Zolota Balka, Shyroka Balka) [Monakhov et al., 1999; Fomin et al., 2003]. Neoproterozoic age objects are represented by gold and uranium deposits of the Ingul megablock (Skhidno-Yurivske gold deposit [Fomin, 1999], Novokostantynivske, Vatu-tinske and Severynivske uranium deposits) [Belevtsev, Koval, 1995]. The total age range of field development is 3200—1750 million years [Fomin et al., 2018; Belevtsev, Koval, 1995; Fomin, Demikhov, 2008]. The numbers assigned to deposits are the same throughout the text.

Deposits of Meso- and Neoproterozoic age (Serednoprivodniprovska megablock of the Ukrainian shield). The formation of Archean gold ore occurrence of the Surska and Chertomlytska green-stone structures of the Serednoprivodniprovska granite-green-stone region occurred in several stages, including volcanogenic, regional-metamorphic and hydrothermal stages, which is recognized by all researchers [Letnikov, 1982; Holland, 2002; Valley et al., 2005; Lyons et al., 2014; Bekker, 2015]. The most important industrial Mesoarchean gold mining processes are associated with two stages: volcanogenic and hydrothermal. Mesoarchean stages are associated with The volcanogenic stage *gold-containing pyrite ores of the Sergiivske Deposit (No. 1) of the Sur structure and Au-Bi-Te ores of the Sergiivske deposit and the Zolota Balka of the Surska structure (No. 2)* [Letnikov, 1982; Holland, 2002; Bekker, 2015]. With a hydrothermal stage, Meso-Neoproterozoic *Au-Fe ore from the Shyroka Balka deposit (No. 3) and Au-Ag-Pb-Zn ores of the Shyroka Balka Deposit (No. 4)*

[Holland, 2002; Lyons et al., 2014; Fomin et al., 2018].

1. *Gold-containing pyrite ores of the Sergiivske deposit of the Surska structure* (No. 1) belong to typical primary (dometamorphic) ores associated with solfatarum-fumarole activity during the formation of an ore-containing essentially volcanogenic conk series of Meso- Neoproterozoic age [Fomin et al., 2017]. The age of ores is determined (3128—3042, but not later than 3000 million years) [Stein et al., 1998; Fomin et al., 2017].

2. *Au-Bi-Te ores of the Sergiivske and Zolota Balka deposits (Surska structure)* (No. 2) in the areals of amphibole metasomatites and berezitiv, lysvtvinitov. Amphibol (actinolite-tremolite) metasomatites in the studied sections are developed along thin-band Quartz-chlorite-carbonate shales with talc and sericite among metabazites. The process of formation of these ore formations lies in the range of 3000—2800 million years [Korzhev et al., 1994; Monakhov et al., 1999].

3. *Au-Fe ore of the Shiroka Balka deposit of the Chortomlitsky structure* (No. 3) are mainly associated with the metabasite-quartzite-shale formation in areas of maximum facial heterogeneity and tectonic disturbances. These are mainly tectonites (cataclysms and breccias) of ferruginous quartzites and shales located among metabazites, in areals of colored larch-berezites. The age of these ores, if limited by the time of manifestation of regional metamorphism and the intrusion of Tokovo alkaline granitoids [Korzhev et al., 1994], can be taken as 3000—2700 million years.

4. *Au-Ag-Pb-Zn ore of the Shiroka Balka deposit of the Chortomlytsky structure* (No. 4). The characteristics of ores, in general, are similar to the previous ones: the host rocks are represented by metabasites that have undergone cataclysms and crushing in areas of rock competence change, metamorphism of green-shale-epidot-amphibolite facies, as well as subsequent activation of the system. In ore-containing rocks, two different-age galenite generations are observed, the isotopic ages of which are approximately 3000 and 2550 million years, respectively [Monakhov et al., 1999; Fomin et al., 2007]. Berezites asso-

ciated with the activation of the system, which control industrial Au polymetallic mineralization at this site, do not show the influence of metamorphism [Fomin et al., 2007].

Deposits of Paleoproterozoic age (Ingul megablock of the Ukrainian shield) belong to the pneumatolite-hydrothermal type.

5. *Au-Quartz ores of the Skhidno-Yuriivsky deposit* (No. 5). The thickness containing ore is represented by gneisses of the checheliivska suite — biotite with graphite, garnet and cordierite, as well as skarnoids (due to marl layers) diopside-amphibol with carbonate and chlorite. The isotopic age of mineralization determined from galenite is 2000 million years [Fomin, 1999; Fomin, Demikhov, 2006].

6. *Novokostantynivske uranium deposit* (No. 6). Mineralization occurs in biotite and biotite-garnet and trachytoid granites in the northern part of the Novoukrainsky massif. The isotopic age of the deposit's ores is determined by various minerals as 1835—1800 million years [Belevtsev, Koval, 1995].

7. *Vatutinske uranium deposit* (No. 7), it is located in the Western frame of the Novoukrainsky massif. Mineralization occurs among migmatites and alaskite-like granites of the Kirovograd type, with the participation of individual layers of gneiss. The isotopic age of uranium ores is close to 1800 million years [Belevtsev, Koval, 1995].

8. *Severynivske uranium deposit* (No. 8). It is located in the eastern frame of the Novoukrainsky massif. Mineralization occurs in a heterogeneous Granito-migmatite-gneiss thickness, with a predominance of migmatites. The isotopic age of uranium mineralization is defined as 1750 million years [Belevtsev, Koval, 1995].

The results obtained and their discussion.

Results of isotope-geochemical study of gold and uranium deposits (aged 3128—1750 million years) of two megablocks of the Ukrainian shield, which included the study of the ratios of carbon isotopic composition $\delta^{13}\text{C}$ and molar fraction CO_2 the mineral-forming fluid GLI in minerals is shown in the figure. As can be seen from these data, there is a significant difference in the composition of the mineral-forming fluid of Meso-Neoproterozoic

and Paleoproterozoic deposits. In Archean deposits molar fraction of CO_2 significantly higher (0.01—0.64 units). In Paleoproterozoic deposits molar fraction of CO_2 (0.006—0.23 units). That is, in the fluid of Paleoproterozoic deposits, in comparison with Meso- and Neoproterozoic, there is a decrease in the CO_2 content almost three times. In Paleoproterozoic deposits, compared to Archean deposits, the proportion of the organic component in the fluid is significantly higher, as indicated by significantly lower values of $\delta^{13}\text{C}$ (up to 26.0 ‰) are characteristic of organic matter. The increase in the Paleoproterozoic organic component in the CO_2 mineral-forming fluid probably occurred due to the oxidation of organic matter due to the increase in the oxygen content in the atmosphere due to the

appearance of photosynthesis. As can be seen from the figure, the fluid of Mesoarchean deposits (No. 1, 2) is characterized by maximum, and Paleoproterozoic deposits (No. 5—8) by minimum values of the molar fraction of CO_2 , whereas in the fluid of Meso-Neoproterozoic deposits (No. 3, 4), the CO_2 content covers the entire range of values of the molar fraction of CO_2 .

Earlier it was noted that the evolution of the gas composition of the atmosphere at the turn of the Archean-Proterozoic led to changes in the endogenous processes of ore and mineral formation [Fomin et al., 2018; Goncharuk et al., 2019], and reducing the content CO_2 in the hydrothermal mineral forming fluid it coincided with the formation of carbonates in the Paleoproterozoic [Demikhov et al.,

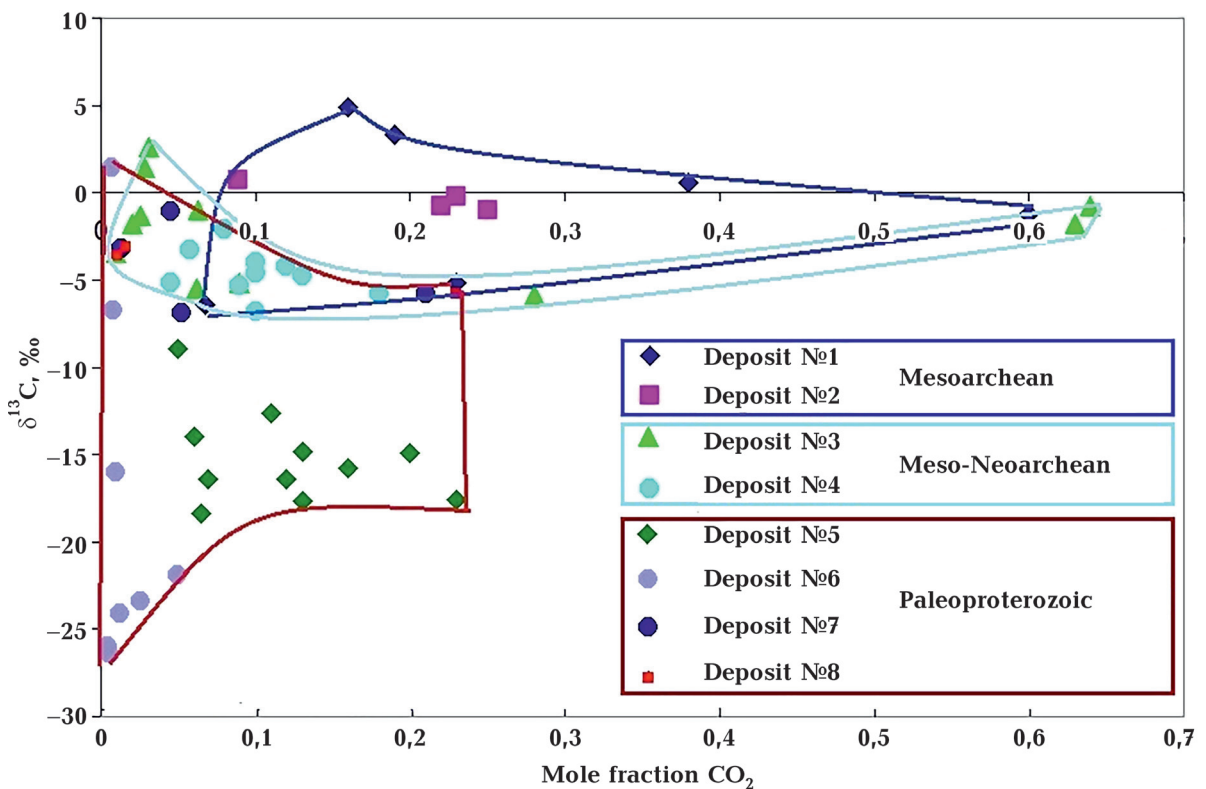
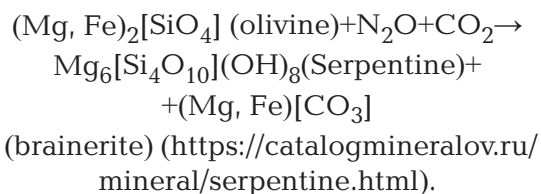


Figure. Ratio of molar fraction CO_2 values and $\delta^{13}\text{C}$ fluid inclusions in minerals of Precambrian gold and uranium deposits of the Ukrainian shield. The lines limit the fields of deposits of different ages. Field numbers correspond to *Mesoarchean*: 1 — Sergiivske deposit, Au-pyrite type of ores, Surska structure, 2 — Sergiivske and Zolota Balka deposits, Au-Bi-Te type of ores, Surska structure. *Meso-Neoproterozoic*: 3 — Balka Shyroka, Au-Fe ore type, Chortomlytska structure, 4 — Balka Shyroka, Au-Ag-Pb-Zn ore type, Chortomlytska structure; *Paleoproterozoic* (Ingul megablock): 5 — Skhidno-Yuriivske deposit, (Au) low-sulfide gold-quartz formation, 6 — Novokostantynivske field (U), 7 — Vatutinske field (U), 8 — Severynivske field (U).

2020]. As can be seen from the obtained data (Figure), the decrease in CO₂ concentration in the mineral-forming fluid occurred in the Neoproterozoic, that is, before the beginning of the increase in oxygen content in the atmosphere and the formation of Paleoproterozoic carbonates stratas.

According to the figure reduction of the molar fraction of CO₂ the mineral-forming fluids of the Balka Shyroka (No. 3) ore of the Chortomlytska structure began in the Neoproterozoic no later than 2700 million years, which are confirmed by data for the Au-Ag-Pb-Zn ores of the Balka Shyroka (No. 4) ore of the Chortomlytska structure in the fluid of which the content of carbon dioxide is not higher than in the fluid of Paleoproterozoic deposits. That is, a decrease in the Neoproterozoic the number of CO₂ in the mineral-forming fluid, it cannot be associated only with the beginning of the development of oxygen photosynthesis in the Paleoproterozoic during the «Great Oxygen event». We believe that an equally important influence on the reduction of the molar share of CO₂ there were changes in the interaction of the crust and mantle in Neoproterozoic and as a result changes in the conditions of sedimentogenesis [Korzhev, Fomin, 1992; Fomin, Demikhov, 2008; Lisichenko, Verkhovtsev, 2014; Verkhovtsev, Yaroshchuk, 2017], in particular, the processes of exo- and endogenous hydration of the ultramafic protocrust during its transformation into the protocontinental cortex.

According to geological and paleomagnetic data the first supercontinent Kenorland appeared in the Archean [Som et al., 2012]. And the presence of continents similar to modern ones became commonplace about 2.7—2.8 billion years ago [Som et al., 2012; Reimink et al., 2021]. It is known that the hydration of ultramafic rocks is accompanied by the absorption of carbon dioxide and its binding in carbonates by reaction:



The appearance of continents in the presence of a hydrosphere initiated the processes of chemical reporting on their surface and binding of atmospheric CO₂ in hypergenesis products. The rate at which carbon dioxide is removed from the atmosphere by converting silicates to carbonates depends on the land area, tectonic activity, and temperature of the outer shells.

Removing carbon dioxide from the atmosphere could lead to a drop in overall atmospheric pressure, and, according to the authors [Menzies, Meer, 2018; Chumakov, 2010], to a sharp cooling and the occurrence of the first ice ages in the history of the Earth (Huron about 2.9; 2.4—2.2 and Kimberly 1.8 billion years ago).

Regarding atmospheric pressure in the Precambrian, there are rather contradictory estimates. According to [Hayashi et al., 1979] Earth's primordial atmosphere was captured by our planet's gravitational field directly from the protoplanetary cloud during the planetary accretion process. It is assumed that in this case the mass of such an atmosphere could reach 10²⁵—10²⁶ g, that is, the mass of the continental crust is 2.25·10²⁵ g (!), and the pressure at the Earth's surface is much higher than 10⁴ bar (atm).

Assessment by O.G. Sorokhtina [Sorokhtin, Ushakov, 2002] if all carbon dioxide were released from the carbonates of the Earth's crust, then its partial pressure in the atmosphere would now reach 90—100 atm, that is, the atmospheric pressure would be the same as on Venus. However, according to the assessment of the same O.G. Sorokhtyn [Sorokhtyn, Ushakov, 2002] in reality the pressure was 6 atm at the time of 2700 million years, and by 2500 million years it had dropped to approximately 1 atm.

The authors of the study of Raindrop prints in tuffs of the Ventersdorp supergroup, South Africa, limit the surface density of air at the time of 2.7 billion years to a level that was at least twice as low as the current level [Som et al., 2012], that is, the atmospheric pressure did not exceed 0.5 atm.

Hydration of ultramafic rocks is accompanied by the absorption of carbon

Molar fraction of CO₂ in the mineral-forming fluid of Archean deposits.

Deposit number	Age of the deposit million years old	Molar fraction of CO ₂ , units		Estimation of atmospheric pressure from the literature, atm
		Maximum values	Average values	
Deposits were not studied	4500	—	—	10 ⁴ [Hayashi et al., 1979]
	>3000	—	—	90—100 [Sorokhtin, Ushakov, 2002]
1	3200	0.60	0.23	—
2	3000—2800	0.25	0.20	—
3	3000—2700	0.64	0.171	6 [Chumakov, 2010]; 0.5 [Taylor, 1974]
4	3000—2550	0.18	0.100	1 [Chumakov, 2010]
5	2000	0.23	0.120	—
6	1835—1800	0.05	0.015	—
7	1800	0.21	0.071	—
8	1750	0.23	0.092	—

dioxide and its binding in carbonates [Sorokhtin, Ushakov, 2002]. This should explain the relatively rapid removal of carbon dioxide from the atmosphere and the drop in total atmospheric pressure from 6 atm and temperatures from +50...+60 °C in Archean up to about 1 atm and +6...+7 °C at the beginning of the early Proterozoic.

As Taylor showed [Taylor, 1974], in modern waters, and we [Demikhov et al., 1997] in ancient geo- and hydrothermal waters, the meteor component prevails. The saturation of meteor water with carbon dioxide depends on its concentration in the atmosphere and atmospheric pressure. Molar fraction of CO₂ in the fluid (table) for 3200—1750 million years, it fluctuated with the trend of general decrease in average values by 11.4 times (from 0.171 to 0.015) and in maximum values by 12.8 times (from 0.64 to 0.055 molar fractions of CO₂), which correlates with a 12-fold decrease in atmospheric pressure during this period (from 6 to 0.5 atm) according to [Sorokhtin, Ushakov, 2002; Som et al., 2012]. This suggests a relationship between these phenomena. Since the composition of hydrotherms significantly depends on the meteor component, we believe that the probable cause of the decrease in carbon dioxide content in the hydrothermal fluid of the Precambrian is the processes of exogenous and endogenous hydration of ultramafic rocks during the formation of the primary protocontinental crust, which caused

a decrease in carbon dioxide content first in the atmosphere and indirectly in hydrothermal ore systems that were formed in the epizone crust.

Conclusions. 1. It is established that the hydrothermal fluid of Mesoarchean deposits is characterized by maximum, and Paleoproterozoic deposits by minimum values of the molar fraction of CO₂, while in the fluid of Meso-Neoarchean deposits, the CO₂ content covers the entire range of values of the molar fraction of CO₂. CO₂ content in the fluid, it decreased by a total of 11.4—12.8 times over the course of 3200—1750 million years, which correlates with estimates of a 12-fold decrease in atmospheric pressure during this time.

2. A decrease in the carbon dioxide content in the hydrothermal mineral-forming fluid of the Precambrian occurred in the Neoarchean, that is, earlier in the Paleoproterozoic, the oxygen content in the atmosphere (the Great Oxygen event) and earlier the formation of huge deposits of carbonates. This decrease is probably due to the processes of exogenous and endogenous hydration of ultramafic rocks during the formation of the primary protocontinental crust.

3. In Proterozoic deposits compared to Archean deposits in hydrothermal fluid molar fraction of CO₂ and δ¹³C are lower, and the proportion of the organic component is higher.

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Еволюція складу гідротермального мінералоутворювального флюїду рудних родовищ у ранньому докембрії Українського щита

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Мета дослідження, результати якого викладені в даній статті, — вивчення змін у складі гідротермальних флюїдних рудних систем раннього докембрію на прикладі

золоторудних та урановорудних родовищ Українського щита у зв'язку з еволюцією екзо- і ендегенних процесів у зовнішніх оболонках Землі. Застосована методика — комплексне ізотопно-геохімічне дослідження складу газопо-рідких включень гідротермального флюїду рудних систем. На підставі експериментальних ізотопно-геохімічних досліджень флюїду газопо-рідких включень у мінералах докембрійських родовищ урану і золота Середньопридніпровського і Інгульського мегаблоків Українського щита встановлена послідовна зміна кількісного та ізотопного складу гідротермальних флюїдів мінералоутворення від мезоархею до палеопротерозою. Досліджено вміст H_2O і CO_2 та ізотопний склад вуглецю CO_2 флюїду в кварці, піриті і польовому шпаті. Віковий діапазон досліджуваних родовищ — 3200—1750 мільйонів років. Зменшення вмісту вуглекислого газу в гідротермальному мінералоутворювальному флюїді докембрію відбулося в неоархеї, тобто раніше Великої кисневої події (Great Oxidation Event), — збільшення в палеопротерозої вмісту кисню в атмосфері, ймовірно, пов'язане з процесами екзогенної та ендегенної гідратації ультраосновних порід при формуванні протоконтинентальної кори. Молярна частка CO_2 в мінералоутворювальному флюїді докембрію певною мірою корелює з атмосферним тиском. Вміст ізотопу вуглецю-12 у палеопротерозої в мінералоутворювальному збільшився в результаті окиснення органічної речовини при збільшенні вмісту кисню в атмосфері.

Ключові слова: архей, протерозой, золоторудні і урановорудні родовища, Український щит, Середньопридніпровський і Інгульський мегаблоки, протоконтинентальна кора, гідротермальний флюїд, ізотопний склад.