Geochemical Trace of Silicon Isotopes of Intrusions and Ore Veins Related to Alkali-rich Porphyry Deposits in Western Yunnan, China

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Abstract   Western Yunnan is the well-known polymetallic province in China. It is characterized by copper-gold mineralization related to Cenozoic alkali-rich porphyry. This paper analyzes the silicon isotope data obtained from four typical alkali-rich porphyry deposits based on the dynamic fractionation principle of silicon isotope. The study shows that the ore materials should originate mainly from alkali-rich magmas, together with silicon-rich mineralizing fluids. The process of mineralization was completed by auto-metasomatism, i.e. silicon-rich mineralizing fluids (including alkali-rich porphyry and wall-rock strata) replaced and altered the country rocks and contaminated with crustal rocks during the crystallization of alkali-rich magmas. Such a process is essentially the continuance of the metasomatism of mantle fluids in crust's mineralization. This provides important evidence of silicon isotopic geochemistry for better understanding the mineralization of the Cenozoic alkali-rich porphyry polymetallic deposits

Key words: alkali-rich porphyry deposit, intrusion and ore vein, silicon isotopic dynamic fractionation, geochemical trace, Cenozoic era in western Yunnan

1 Introduction

Western Yunnan, closely neighboring on the east margin of the Qinghai-Tibetan plateau, is a Cenozoic intracontinental deformed region with well-developed polymetallic mineralization associated intimately with juvenile magmas and fluids. Some of the most important depots of this region are alkali-enriched porphyry deposits located in the eastern Jinshajiang-Ailaoshan fracture belt, including the Machangqing Cu-Mo-Au deposit and Jinchangqing Au deposit in Xiangyun, and the Bei'ya Pb-Au and Yao'an Pb-Ag-Au deposits in Heqing. We have studied the composition features of the silicon isotopes of the above four deposits as well as the ultramafic hypoxenoliths from aegirinite syenite porphyries occurring in Liuhe Village, Heqing County, Yunnan Province (Liu et al., 1999), and inferred the ore sources and metallogenic mechanisms based on the dynamic fractionation principle of silicon isotopes.

2 Geological and Mineralizing Features of Alkali-rich Porphyry

Generally, the alkali-rich porphyry deposits in this area have the following geological features: orebodies are controlled by structures and occur as veins or disseminated veinlets in porphyries, contact zones between porphyries and country rocks, and country rocks. As the ore-formation temperature changes as high → medium high → medium low → low, the formed ore type is Mo → Cu-Mo → Pb-Zn-Fe → Au-Ag. Thus a sequential metallogenic effect can be seen, i.e. from intrusives through contact zones to country

rocks, high-temperature metallization will transit to low-temperature metallization (Liu et al., 2002). Alterations of country rocks in the deposits include silication, pyritization-phyllic alteration, epidotization, chloritization, ferritization and so on. Skarnization occurs in the contact zone between porphyry and carbonate rocks in the Bei'ya Pb-Au deposit in Heqing, accompanied by such alterations as intense silication and hematitization. Potash metasomatism in alkali-rich porphyry is characterized by altered orthoclase and sericite. Different mineralizations are controlled by integrate factors such as magma, structure and lithology of the country rocks. In particular, Pb and Ag metallization are dominant in potash-rich syenite porphyries, mainly Cu (Mo) and Au metallizations are seen in potash-rich intermediate-acid quartz monzonite-porphyry and granodiorite-porphyry. The Yao'an intrusion is characterized by high alkali, low Ca, Mg and Fe and medium acidity, thus favorable for the formation of Pb, Ag and Au ores. A remarkable controlling effect of structures on petrogenesis and mineralization can be seen: the large-scale Jinshajiang-Ailaoshan deep fault is a first-class structure, serving as a passageway for ore materials and fluids in the mantle or deep crust, and other secondary structures, such as folded belts, intersections of fractures and anticlines, fissures in intrusiive bodies, contact zones, interstratified flexure fractured zones, as well as lithological enclosed conditions are all host structures to some extent. In addition, components of hot mineralizing fluids were reformed inevitably to a certain extent through the reaction between the fluids and country rocks. For this reason, in a fluid process country rocks can partly provide ore materials, but they are not the main source. Alkali-rich

magma and accompanied upper-mantle fluids, which moved along the passageway of large-scale deep faults, are main sources of ore materials for the alkali-rich porphyry deposits.

In the deposits, there are four characteristic minerals related to petrogenesis of alkali-rich magma and fluid processes. (1) Feldspar phenocryst, which was formed in the diagenesis of alkali-rich magma, is a primary mineral. (2) Silicated quartz, which was formed in metasomatism of silicon-rich mineralizing fluid accompanied by alkali-rich magma, is an altered mineral. (3) Hemimorphite {Zn_4 (H_2O) [Si_2O_7] $(OH)_2$}, which was probably derived from primary sphalerite to be reformed by silicon-rich mineralizing fluid and accompanied with relict primary galena, is a water-rich secondary zinc-silicate mineral. Therefore, silicated quartz and hemimorphite could represent silicon-rich mineralizing fluids. (4) Ca-Cr-pyralspite, which exists in skarnization to be produced in the Bei'ya intrusion, is an obvious late-stage altered mineral formed after the diagenesis, and could represent late-stage altered fluids.

3 Composition Characteristics of Silicon Isotopes

Geochemistry of silicon isotopes is a newly developed field in the research of stable isotopes. Up to now, silicon isotopes have been more effective and reliable in tracing ore materials and studying the geneses of rocks and

deposits due to the improved precision of measurement data (Ding et al., 1994). Silicon isotope compositions of alkali-rich porphyries, feldspar and quartz phenocrysts, and altered rocks and characteristic minerals related to mineralization are measured for the typical deposits in this area.

Sample preparation and measurement were described by Li (1992) and Ding et al. (1994), and the results are demonstrated in Table 1 and Fig. 1, which show the following features and regularities.

(1) Silicon isotope compositions vary greatly for different types of samples. For exsample the $\delta^{30}Si$ values of mineralization porphyry are 0.3‰–0.5‰, coinciding basically with those of alkali-rich porphyry and lamprophyre (0.0‰–0.4‰); the $\delta^{30}Si$ values of silicated quartz and hemimorphite (representing primary mineralization of silicon-rich mineralizing fluid and mantle fluid metasomatism) are from −0.1 to −2.4, being obviously different from those of alkali-rich porphyry and lamprophyre (0.0–0.4).

(2) It is normal that silicon isotope compositions of the country rocks are different in different layers. Yet, it is important that the $\delta^{30}Si$ value of the alkali-rich porphyry and that of the country rocks are quite different in the Yao'an and Machangqing intrusives, the former is 0.0‰ −0.1‰, while the latter −0.2‰.

(3) The $\delta^{30}Si$ values of the feldspar phenocryst and those of the country rocks are close to each other in the Bei'ya intrusion (0.4‰ and 0.7‰ respectively), while the

Table 1 Composition of silicon isotopes of the alkali-rich porphyry, altered rocks and characteristic minerals from the representative deposits in the study area

Ser. No	Sample No	Rock or mineral	$\delta^{30}Si$	Sample occurrence
1	MM-9-2	Quartz phenocryst	0.1	Biotite quartz monzo-porphyry
2	MM-32-1	Silicated quartz	−0.1	Cu Mo-bearing quartz vein
3	MM-30	Lamprophyre dike	0.4	in monzo-porphyry
4	MM-15	Mineralization sandstone	0.4	Au-bearing strata country rock
5	MM-16	Siltstone	−0.2	Strata country rock (O_1)
6	HL-81	Aegirinite syenite-porphyry	0.0	Deep xenoliths-bearing host rock
7	A-328-2	Feldspar phenocryst	0.4	Syenite-porphyry
8	HB-55-3	Hemimorphite	−2.4	Pb Zn-bearing altered rock
9	HB-56-7	Ca-Cr-pyralspite	0.3	Skarnization porphyry
10	HB-56-3	Siltstone	0.7	Strata country rock (T_1)
11	YAJ-8	Syenite-porphyry	0.0	Host rock-body
12	YAJ-13	Mineralization porphyry	0.3	Au-bearing altered porphyry
13	YAJ-27	Mineralization sandstone	0.5	Au-bearing altered sandstone
14	YAJ-29	Siltstone	−0.2	Strata country rock (K_2)
15	XJ-37-2	Quartz phenocryst	0.0	Quartz syenite-porphyry
16	XJ-39-1	Silicated quartz	−0.2	Au-bearing quartz vein

Note: Samples 1–5 from the Machangqing deposit; sample 6 from the Liuhe intrusion; samples 7–10 from the Beiya deposit; samples 11–14 from the Yaoan deposit; samples 15–16 from the Jinchangqing deposit. Analyzed by Wang Defang of the Institute of Mineral Deposit, Chinese Academy of Geological Sciences (analytic precision >0.1‰).
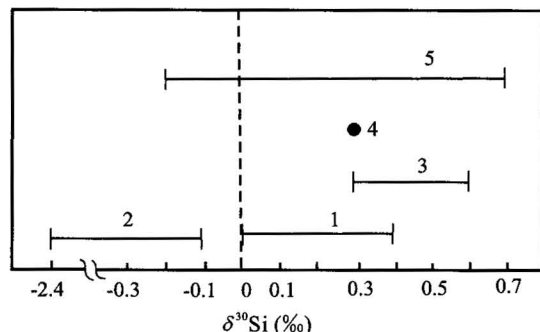
.Fig. 1. Diagram showing the distribution of silicon isotope compositions of alkali-rich porphyry, altered rocks and characteristic minerals from the typical deposits in the study area.

1. Alkali-rich porphyry and lamprophyre (containing feldspar and quartz phenocryst); 2. silicated quartz and hemimorphite; 3. mineralization porphyry and sandstone; 4. skarnization porphyry; 5. country rocks (L. Ordovician, L. Triassic, U. Cretaceous).

δ^{30}Si values of the silicated quartz and those of the country rocks are close to each other in the Machangqing intrusion (–0.1‰ and –0.2‰ respectively).

(4) The δ^{30}Si values (0.3‰–0.5‰) of the mineralizing altered rocks, such as mineralizing porphyry, skarnization porphyry and mineralizing sandstone, are close to the δ^{30}Si values (0.0‰–0.4‰) of the alkali-rich porphyry and lamprophyre.

(5) The alkali-rich porphyry and lamprophyre have the same magma source area for they have similar silicon isotope compositions. However, the latter is probably not related to mineralization in this area because it occurs as only very little late-stage dikes.

4 Dynamic Fractionation Mechanism of Silicon Isotopes

According to the study of Ding et al. (1994), the range of silicon isotope compositions is smaller than that of sulfur, carbon and oxygen isotopes in thermodynamic fractionation of isotopes because silicon exists in the form of tetrahedrons of silicon and oxygen connection, and its valence does not change in nature. But dynamic fractionation is the main reason for the obvious variation of silicon isotope compositions during the precipitation of silica in solution. According to experimental study, Ding et al. (1994) discovered the phenomenon of dynamic fractionation during the precipitation process of hydrothermal silica solution under normal temperatures. Precipitated silica at the beginning has the lowest value of δ^{30}Si, then the value becomes larger as the portion of precipitated silicon is increased, and finally the δ^{30}Si value becomes a large positive value. In addition, the more quickly silicon precipitates, the less the dynamic fractionation of silicon isotopes. On the contrary, when

temperatures are relatively high and the precipitation velocity of silica is slow, dynamic fractionation of silicon isotopes will be larger, while when temperatures are relatively low, its fractionation can reach the maximum value in siliceous hydrothermal solution. The results are controlled by the mechanism that dissolved silica contains more δ^{30}Si than precipitated silica. In other words, the results are defined by the principle that light isotopic molecules ($H_4^{28}SiO_4$) always precipitate earlier than heavy molecules ($H_4^{30}SiO_4$), and the isotopes of the precipitated silica from the solution do not exchange with the isotopes of dissolved silica in solution any more.

The δ^{30}Si value of the primary earth is –0.5‰ during the magmatic process. From basic to acid rocks, the δ^{30}Si values change from low to high. The former is close to the one of the primary earth, but the latter is from –0.2‰ to 0.0‰. δ^{30}Si of rocks is affected by their differentiation degree in diagenetic evolution, the lower differentiation degree of rocks, the lower the value of δ^{30}Si, and vice versa.

Abundant existing evidence suggests that silicon first precipitated from erupted siliceous hydrothermal solution is always characterized by a negative δ^{30}Si value, which has been demonstrated by many examples. Taking the Tengchong thermal spring in Yunnan Province for example, the δ^{30}Si value of quartz veins, sinters and spring water are –0.6‰, –0.1‰ and 0.3‰ respectively (Ding et al., 1994), which is the result of inevitable dynamic fractionation of silicon isotopes following successive precipitation of silica in solutions.

Douthitt's study revealed (1982) that δ^{30}Si of dissolved silica is not related to the silicon content in solution. Furthermore, it is not related to solution temperature as it ranges from 75 to 275°C. This suggests that δ^{30}Si of dissolved silica in a hydrothermal system is likely controlled by the source of the silica. The above discussion proves from different angles that the distinction of δ^{30}Si between the host rocks and ore-forming siliceous hydrothermal solutions indicates different sources of siliceous substances.

5 Analysis of Geochemical Tracing

Based on the above features of silicon isotopic components and the principle of silicon isotopic dynamic fractionation, preliminary geochemical tracing analysis can be done for the sources of ore materials and fluids of alkali-rich porphyry type deposits.

(1) The values of δ^{30}Si of silicated quartz and hemimorphite (from –0.1‰ to –2.4‰), representing silicon-rich mineralizing fluids, are obviously different from those of alkali-rich porphyry and lamprophyre (0.0‰ –0.4‰). This could suggest that there are two sources of

ore materials. One is alkali-rich magma and the other is silicon-rich mineralizing fluids. Their source areas are somewhat different. Study of REE and isotopes from relevant samples indicates that alkali-rich magma, which was derived from a source in enriched mantle formed by mantle metasomatism, is characterized by high positive silicon isotope values after intense dynamic fractionation, and that silicon-rich mineralizing fluids, which have the nature of primary mantle, are characterized by low negative silicon isotope values with almost no dynamic fractionation.

(2) The δ^{30}Si values (0.3‰–0.5‰) of mineralizing porphyries and sandstones are higher than those (0.0‰ –0.4‰) of alkali-rich porphyries and lamprophyre even if they basically coincide. This suggests that that the mineralizing rocks are the products of (auto-) metasomatism, that is, silicon-rich mineralizing fluids replaced alkali-rich porphyries and the country rocks. As a result, the mineralizing rocks have more intense silicon isotopic dynamic fractionation than the alkali-rich porphyries, and the nature of the silica is changed from silicon-rich mineralizing fluid to porphyry and to country rocks.

(3) In the Bei'ya and Machangqing intrusions, the δ^{30}Si values of feldspar phenocrysts and silicate quartz are close to those of the country rocks. However, this does not indicate that they have the same source of siliceous substance. This can be explained by the fact below.

If silica is leached from the country rocks and precipitated quickly through crust hydrothermal solution, there might no obvious fractionation of silicon isotopes between dissolved silica and precipitated silica, but has basically the same values of δ^{30}Si according to the principle of the dynamic fractionation of siliceous isotopes. However, they (feldspar phenocrysts, silicated quartzes and stratigraphic rocks) have their own sources of siliceous substances. The δ^{30}Si values of feldspar phenocrysts (0.0‰–0.4‰) and silicated quartz (–0.1‰–2.4‰) have their specific distribution range and do not vary with the strata. The former represents alkali-rich magma, while the latter represents silicon-rich mineralizing fluid. However, the δ^{30}Si values of stratigraphic rocks are changed with stratigraphic horizons and lithology. For this reason, the fact that stratigraphic rocks, alkali-rich porphyries and silicated quartz have close or basically the same δ^{30}Si values does not indicate that they have the same source of siliceous substance.

(4) The above discussion shows that alkali-rich magma was derived from the source area of enriched mantle, but that its silicon isotope composition is totally different from that of meteorites and moonrock . This suggests that mantle metasomatism leads to violent inhomogeneity of silica isotopes in the upper mantle, especially in areas within the continental plate where alkali-rich magmatism is intense.

The silicon-rich mineralizing fluid is a continuation of the metasomatism of mantle fluids in the mineralization process in the crust.

To sum up, ore materials of the polymetal deposits of alkali-rich porphyry type in this region were mainly derived from alkali-rich magma and associated silicon-rich mineralizing fluid. These two kinds of fluids resulted from differentiation of enriched mantle formed by mantle metasomatism, and carried ore materials to the crust along large-scale deep faults. During the formation of alkali-rich magmas, silicon-rich mineralizing fluids tend to replace and alter the country rocks, including alkali-rich porphyry and stratigraphic rocks, and to be contaminated with crustal rocks, thus forming ore deposits. The mineralizing process of silicon-rich fluids is essentially a continuation of metasomatism of mantle fluids during mineralizing processes in the crust. It is the action of fluids that is the internal constraint on the widespread Cenozoic mineralization and an important geochemical background for the formation of large and superlarge deposits in this region.

Acknowledgement

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