

Chromium element and isotope geochemistry in high temperature systems

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Abstract: In the past two decades, research on stable Cr isotopes, especially in the low-temperature redox processes on the Earth's surface, has been greatly developed. However, in the same period, Cr isotope fractionations induced by high temperature processes had been poorly constrained, especially before 2010. With the improvement of mass spectrometry technology and the wide application of the double-spike method, smaller isotope fractionations in high temperature processes can be accurately identified. This review will give a detailed introduction to the distribution behavior of Cr element and Cr isotope fractionation behavior in high temperature processes achieved in recent years, and potential applications, aiming to provide feasible directions for future researches of Cr element and isotope system.

Key words: chromium element and isotope; high temperature processes; isotope fractionation; oxygen fugacity; planetary evolution

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高温体系中Cr元素和同位素地球化学

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摘要: 近十多年来,对于 Cr 稳定同位素的研究,尤其是在地表低温氧化还原过程中的研究得到了极大的发展.但是,在同一时期,对于高温过程中 Cr 同位素的研究却出现停滞不前的现象.随着质谱分析技术的提升和双稀释剂方法的广泛应用,使得高温过程中较小的同位素分馏可以被精确识别.详细介绍了近年来 Cr 元素和同位素在高温过程中的分配和分馏行为的研究进展,并对其潜在的应用进行展望,希望对 Cr 元素和同位素体系在未来的研究中提供可行的方向.

关键词: 铬元素和同位素;高温过程;同位素分馏;氧逸度;行星演化

0 Chromium element geochemistry

0.1 Chemical properties of chromium

Chromium (Cr) is a transition metal element of the sixth subgroup (VIB) of the fourth period in the periodic table. Its atomic number is 24, with the average atomic mass of 51.9961 and the outer electron configuration as $3d^5 4s^1$ ^[1]. Chromium has a density of 7.14, a high melting point of 1900 °C, and a stable cubic crystalline structure^[1]. The name “chromium” is sourced from the Greek word of “chroma”, which represents “color” referring to colour materials with chromium components^[2].

Chromium is a redox-sensitive element, which could be stable in +6, +3, +2 and 0 valences on the earth in relation to different oxygen fugacities. Generally, Cr^{6+} and Cr^{3+} are the predominant Cr species in Earth’s near-surface environments according to the prevailing redox potential (Eh) and PH condition^[3]. In Earth’s surface environments, trivalent Cr is often bound with O^{2-} or OH^- to form oxides or hydroxides, which are both immobile and insoluble. By contrast, Cr^{6+} as CrO_4^{2-} (chromate), $HCrO_4^-$ and $Cr_2O_7^{2-}$, are mobile and soluble in aqueous fluids. In crust and mantle rocks, Cr could occur as Cr^{2+} and Cr^{3+} . The Cr^{2+}/Cr^{3+} ratios in the rock-forming minerals have been documented to be dominated by the mineral structure and redox condition^[4-14], and will be discussed in detail in the following section. In Earth’s core, Cr is present as Cr-metal, or Fe-rich intermetallic crystals (e. g., $Fe_{15}Cr$), or sulfide crystals (e. g., CrS , $FeCr_2S_4$)^[15].

0.2 Chromium distribution in primary terrestrial reservoirs

The distribution of Cr in terrestrial reservoirs is mainly controlled by the core-mantle differentiation, partial melting, and various crystallization mineral phases during magma evolutions. The carbonaceous chondrite CI (one of eight major groups of carbonaceous chondrites), is typically used as reference materials for the average composition of planets^[16-18]. The Cr content in the carbonaceous chondrite CI is approximately 2 623 ppm (or $\mu g/g$), while the average Cr content of the bulk planet earth and the mantle is approximately 4 400 ppm and 2 500 ppm, respectively, based on the Mg/Cr ratio correction^[17-20]. According to the mass balance calculation, the content of Cr in the core was estimated to be $\sim 9\ 000$ ppm^[17, 20].

The Cr content in mantle peridotite ranges from more than 1 000 ppm to 10 000 ppm, and is about 2 500 ppm as a whole^[18, 21, 22]. In the mantle peridotite, the main Cr-bearing minerals are clinopyroxene, orthopyroxene, garnet and spinel and other aluminum-containing minerals^[23-24]. Compared with the mantle, the Cr content of the crust is significantly lower. The Cr content of the upper continental crust is usually dozens of ppm, with an average value of about 92 ppm^[25-31]. The middle continental crust has a similar Cr content to that of the upper continental crust, with an average value of about 76 ppm^[26, 31-33]. The lower continental crust is slightly higher in Cr content, with an average value of ~ 215 ppm, due to the fact that the lower continental crust displays more enrichments of mafic rocks than middle and upper continental crusts^[31, 33]. The mid-ocean ridge basalts (MORB) contain ~ 300 ppm Cr^[34], while the Cr content of oceanic island basalt (OIB) varies

from a few ppm to thousands of ppm, most of which are below 500 ppm^[35-37].

The distribution of Cr in various reservoirs on the surface is extremely heterogeneous. The content of Cr in marine sediments is generally low, generally ranging from 1 to 500 ppm^[38-45]. The sandstone has generally 10 to 100 ppm Cr, while Cr contents are 85 to 400 ppm in the shale, and 1 to 3350 ppm in the soil^[38-41]. Cr exists in the form of both Cr³⁺ and Cr⁶⁺ in modern oceans, in which Cr⁶⁺ is predominant, with an average content of 0.05~1 ppb^[42-45].

In summary, the mantle and the core host almost all of Cr in the bulk earth, while the relative proportion of the mantle to the core remains controversial. In contrast, Cr contents in the crust and surface reservoirs are relatively low, and contribute very limited Cr to the bulk earth.

0.3 Partition behaviors of Cr during high temperature processes

The silicate earth is significantly depleted in Cr relative to the carbonaceous chondrite CI, based on the observation that the Cr/Mg ratio (0.0115) of the mantle is only 0.42 of that (0.0275) of the carbonaceous chondrite CI^[17, 20]. A previous study suggested that this may be due to the fact that Cr tends to enter the core in a reduced form during the core-mantle differentiation process^[46], reflecting that most of Cr (above 60%) in the earth may enter the core. According to mass balance calculations, the distribution coefficient D_{Cr} between the core and the silicate earth is proposed to be 2.5 to 3.5 to fit the current Cr content in the mantle^[17, 20, 47, 48]. According to the conditions for satisfying this equilibrium partition coefficient, the dynamics of the initial accretion of the earth accretion, the core-mantle differentiation process and the physical and chemical conditions have been restricted^[18, 46, 48-56]. Current experimental studies have shown that the distribution coefficient of Cr between metal and silicate is mainly controlled by temperature (T), the composition of light elements in the metal phase (C, S, Si, and so on)

and oxygen fugacity (fO_2). The siderophile affinity of Cr becomes stronger, at lower temperatures, and with higher contents of C, S, and Si^[48, 51-57]. In early studies, in order to satisfy the high partition coefficients of Cr and other redox-sensitive elements between metals and silicates, the initial materials of earth accretion were considered to be reducing materials, such as enstatite chondrites. During the later accretion process, the Earth's magma ocean became more oxidized due to late-arriving planetesimals with higher FeO/Fe ratio or the self-oxidation process^[48, 54, 58-60]. An alternative opinion accounting for the Cr partition into the core is that Cr can also have strong siderophile affinity under high oxygen fugacity and high temperature conditions^[56]. This speculation is consistent with the fact that the solubility of O in metals increases with the increase of temperature and pressure, implying that both Earth and Mars may have grown from oxidizing chondrites^[62]. Based on the seismic wave velocity studies on the core with different contents of light elements, Badro et al.^[63, 64] proposed that oxygen is an essential light element in the Earth's core, reflecting that the oxygen fugacity environment during core-mantle differentiation might be higher than previously thought. Although it is still debatable regarding the initial materials and the accretion models of the Earth, the Cr partition behavior between metals and silicates displays a remarkable potential in solving this issue.

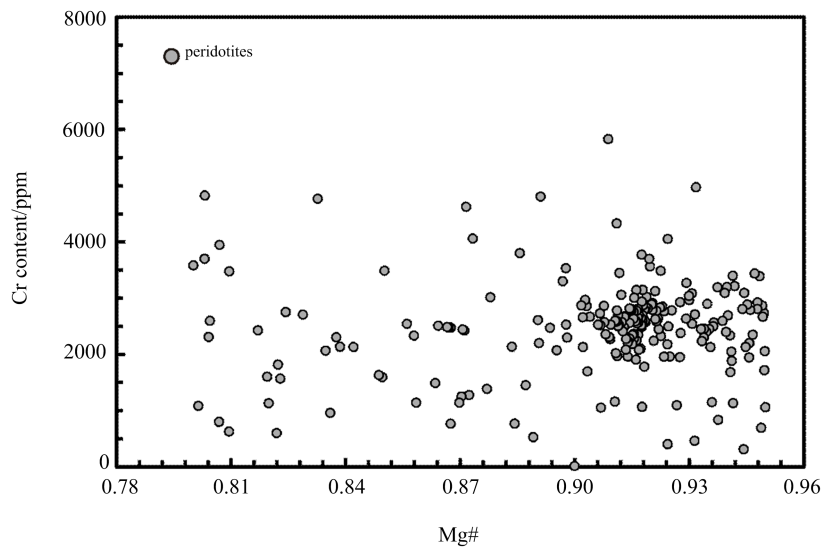
The partition coefficients between rock-forming minerals and silicate melts have been well constrained in previous studies. Early studies mainly focused on the partition behaviors of total Cr (both Cr²⁺ and Cr³⁺) in the mineral-melt system. Generally, except for olivine, Cr is compatible in other major mantle minerals, including clinopyroxene, orthopyroxene, spinel and garnet^[65-72]. As mentioned earlier, Cr mainly exists in +2 and +3 valence forms in silicate minerals and melts, and the oxygen fugacity was

proposed to be capable of controlling the partition coefficients of Cr between mineral and melt. Li et al.^[73] conducted an experimental study that Cr^{2+} preferentially enters into pyroxene and olivine lattices relative to co-existing spinel under high temperature and reducing conditions (at the Cr-CrO buffer) in Fe-free systems. However, Mallmann and O' Neill^[74] obtained that the partition coefficients of Cr^{2+} between minerals and melts are 0.85 ± 0.31 for olivine, 0.84 ± 0.05 for orthopyroxene, 0.58 ± 0.11 or 0.65 ± 0.08 for clinopyroxene, respectively, while $D_{\text{Cr}^{3+}}$ are 0.85 ± 0.31 for olivine, 3.52 ± 0.17 for orthopyroxene, 12.6 ± 0.67 or 8.72 ± 0.38 for clinopyroxene, respectively. The differences might also reflect that the preferential substitutes of Cr^{2+} and Cr^{3+} are distinct in different mineral structures. Spinel, often containing several to tens of percent of Cr in weight, is generally considered to incorporate Cr as +3 valence. Cr species in spinels are always proposed to be in +3 valence over a large oxygen fugacity range^[6]. This speculation is consistent with the XANES analyses of $\text{Cr}^{3+}/\sum\text{Cr}$ ratios ($= 1$) of spinel separates from both the earth mantle peridotites at $f\text{O}_2$ near the FMQ oxygen fugacity buffer^[75], and the lunar basalts at $f\text{O}_2$ of 4~6 log

unit below the FMQ buffer^[14].

Chromium partition behaviors between these minerals and melts might account for the Cr content variation in the mantle peridotites. Previous studies obtained that the Cr contents are relatively constant from refractory to fertile peridotites, independent of the degrees of melt extraction, in other words the whole Cr partition coefficient between the partial melt and the residue is close to approximately 1 (e. g., Fig. 1)^[18, 21]. According to the non-modal melting model^[77], this might be attributed to consumption of Cr-rich pyroxenes and part of spinels to the melts and generations of Cr-depleted olivines in the residues during partial melting of the mantle peridotite. To balance the no net-change of Cr, residual spinels would incorporate more Cr, leading to Cr # in spinels (the molar ratio of $\text{Cr}/(\text{Cr} + \text{Al})$) increasing via the enhanced degree of the partial melting^[78].

During mafic magmatic evolutions, fractional crystallization minerals control Cr content variations. There are two main stages involved, fractional crystallizations of minerals during the upwelling of the initial mantle melt and subsequent magmatic emplacement or eruption. Fractional crystallizations of minerals during the latter process has been well constrained based on



Data are from GEOROC (<http://georoc.mpch-mainz.gwdg.de/georoc/>, accessed on March 10, 2020).

Fig. 1 Whole-rock Cr contents versus Mg# values diagram of global peridotites reflects Cr partition behaviors during partial melting

widespread lavas and intrusions in the Earth's surface. Generally, olivine fractional crystallization could slightly raise Cr contents in melts, while fractional crystallizations of spinels (e. g., chromites) and clinopyroxenes remarkably reduced Cr contents in melts. Sometimes, due to the fact that olivine and spinel are both early crystallization minerals, cumulate minerals and residual melts display a single content drop accompanying decreased MgO contents and Mg number (mole ratio of $\text{Mg}/(\text{Mg} + \text{Fe})$)^[35-36]. It is worth noting that there seems to be a Cr content gap between the initial magma of the investigated mafic rocks and the direct partial melts from the mantle peridotite, the former having Cr contents almost one order of magnitude lower than the latter^[21, 22, 34-37]. This discrepancy could be linked to the fractional crystallization of spinel/chromite during the mantle melt upwelling. Roeder and Reynolds^[79] have conducted experiments focusing on Cr solubility and chromite crystallization in basaltic melts at temperatures of 1200~1400 °C, over a range of oxygen fugacity and pressure of 1 atm and 10 kbar. The solubility is highly dependent on the temperature, considering that the basaltic melt tends to incorporate much less Cr at the lower temperature under the same redox conditions, e. g., Cr_2O_3 contents of silicate glass are 0.573 wt. % at 1400 °C, 0.162~0.168 wt. % at 1300 °C, and ~0.046 wt. % at 1200 °C, respectively, under the oxidized condition ($f\text{O}_2$ of ~-7.6). On the other hand, the oxygen fugacity also controls Cr solubility in melts, e. g., Cr_2O_3 contents of chromite-saturated melts varies from 0.05 wt. % at $f\text{O}_2$ of -3 to 1.4 wt. % at $f\text{O}_2$ of -12.8 under the pressure-temperature condition of 1300 °C and 1 atm, respectively. This observation could explain why mafic rocks formed under the reduced conditions (such as the Moon, Vesta) have higher Cr contents (several thousand ppm) than the terrestrial mafic rocks (several hundred ppm).

In summary, Cr plays an important role in

constraining the Earth's core-mantle differentiation process and in tracing partial melting and magmatic evolution processes, but there remain some problems. The Cr isotope system in the corresponding processes may provide new ideas for solving these problems.

1 Chromium isotope geochemistry

Chromium consists of four stable isotopes (^{50}Cr , ^{52}Cr , ^{53}Cr , and ^{54}Cr) with natural abundances of 4.35%, 83.79%, 9.50%, and 2.36%, respectively^[80]. Within these four isotopes, part of ^{53}Cr is a decay product of the extinct nuclide ^{53}Mn , with a half-life of 3.7 Myr^[81]. Because these short-lived nuclides were produced in supernovae before the formation of the solar system, ^{53}Mn - ^{53}Cr dating system is capable of investigating early evolutions of the solar system^[82-86]. The neutron-rich isotope ^{54}Cr has a mass close to Fe, and is produced in Type Ia and Type II supernovae^[87-88]. Combined with other iron peak element isotopes, such as ^{48}Ca , ^{50}Ti , ^{62}Ni , and ^{64}Ni , these isotope anomalies have been used to trace meteorolite sources and mixing processes^[3, 88-91]. In this paper, we will focus on the stable Cr isotope system. Stable chromium isotope compositions are typically expressed as the permil-difference in $^{53}\text{Cr}/^{52}\text{Cr}$ relative to the National Institute of Standards and Technology (NIST) Standard Reference Material 979 (SRM979), following the delta notation:

$$\delta^{53}\text{Cr} = \left[\frac{\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}} \right)_{\text{Sample}}}{\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}} \right)_{\text{SRM979}}} - 1 \right] \times 1000 \quad (1)$$

Apart from the mass-independent fractionation of Cr isotopes, in recent two decades, researches on mass-dependent fractionations of Cr isotopes also have achieved great development, especially in low-temperature environments. Similar to other multi-valence element isotopes (e. g., Fe, Cu), the redox-related process is currently known as the main factor causing the fractionation of Cr

isotopes. Schauble et al.^[92] calculated that the equilibrium fractionation factor $\Delta^{53}\text{Cr}$ between CrO_4^{2+} and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ at room temperature (25 °C) is 6.6‰, and the fractionation value can reach 7.6‰ at 0 °C. The equilibrium fractionation factor of $\text{Cr}(\text{H}_2\text{O})_6^{3+} - \text{Cr}_2\text{O}_3$ at 25 °C is only 0.4‰. Ellis et al.^[93] also obtained that during reductions from Cr^{6+} to Cr^{3+} by three different reducing agents (intertidal silt, freshwater clay silt and magnetite), the obvious fractionation (3‰~4‰) would occur. Heavy Cr isotopes were partially enriched in residual Cr^{6+} , due to the smaller ionic radius of Cr^{6+} relative to Cr^{3+} . Accompanying changes of the redox environment at low temperatures, the fractionation of Cr isotopes up to parts per mil level occurred. Furthermore, remarkably different mobilities and solubilities of Cr^{6+} and Cr^{3+} , as well as highly toxic of Cr^{6+} ^[94] make Cr isotope an index to trace Cr pollution sources and the degree of reduction after treatments. Thus, the stable Cr isotope system is very useful for tracing the attenuation of Cr contamination in groundwater systems, and reconstructing the ancient atmospheric oxygen evolution under the low temperature condition^[40, 41, 44, 95-123].

Unlike the low-temperature process, Cr isotope fractionations during high temperature geological processes are considered to be limited due the equilibrium fractionation value being theoretically proportional to $1/T^{2[75]}$. Along with the improvement of mass spectrometry technology and the wide application of double-spike methods using both multi-collector thermal ionization mass spectrometry (TIMS)^[88] and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS)^[125-127], the analytical precision has been improved obviously (e. g., $> \pm 0.5\%$, 2SD^[124]; $\pm 0.2\%$ ^[92]; $\pm 0.06\%$, 2SD^[125-126]), making it possible to identify small isotope differences. In the recent decade, more and more works have focused on Cr isotope behaviors in high temperature processes.

In this following, we will focus on advances that have been made in a stable Cr isotope system in high-temperature processes. Mass-independent Mn-Cr isotope dating and ^{54}Cr anomalies, as well as Cr isotope system in low-temperature processes, have been discussed in detail in Refs. [3, 128]. Readers who are interested in these fields are referred to these two reviews.

1.1 The earth mantle and partial melting process

1.1.1 The earth mantle and the bulk silicate earth

As the earth mantle hosts over 99% Cr of the bulk silicate earth (BSE), the Cr isotope composition of the mantle could represent the isotope composition of the BSE. Schoenberg et al.^[125] first studied the Cr isotope compositions of a variety of mantle-derived rocks, including mantle xenoliths, ultramafic rocks, cumulates, and oceanic and continental basalts. The Cr isotope composition ($\delta^{53}\text{Cr}$) of the investigated samples displays a range of -0.21% to -0.02% with an average value of $-0.12 \pm 0.10\%$ (2SD). Subsequently, Schoenberg et al.^[129] conducted repeated analyses on the same samples, and the obtained $\delta^{53}\text{Cr}$ values of peridotites are positively correlated with $\text{MgO}/(\text{MgO} + \text{FeO})$ values. They speculated that partial melting might fractionate Cr isotope, with lighter Cr isotope incorporating into melts, leaving heavier Cr isotope in residues. Xia et al.^[130] systematically analyzed forty-five mantle xenoliths including spinel and garnet facies peridotites, pyroxenite veins, metasomatized xenoliths from central Mongolia, North China, Siberia and Southern Africa. The $\delta^{53}\text{Cr}$ values of these mantle xenoliths range from $-0.51 \pm 0.04\%$ (2SD) to $+0.75 \pm 0.05\%$ (2SD), which might be influenced by partial melting, kinetic fractionation, and secondary alteration. Having eliminated effects of the partial melting and the metasomatism, we obtained the pristine, fertile upper mantle with a Cr isotope composition ($\delta^{53}\text{Cr}$) of $-0.14 \pm 0.12\%$ (2SD) (Fig. 2). Sossi et al.^[131] reported that twenty terrestrial ultramafic samples display the $\delta^{53}\text{Cr}$ value ranging from

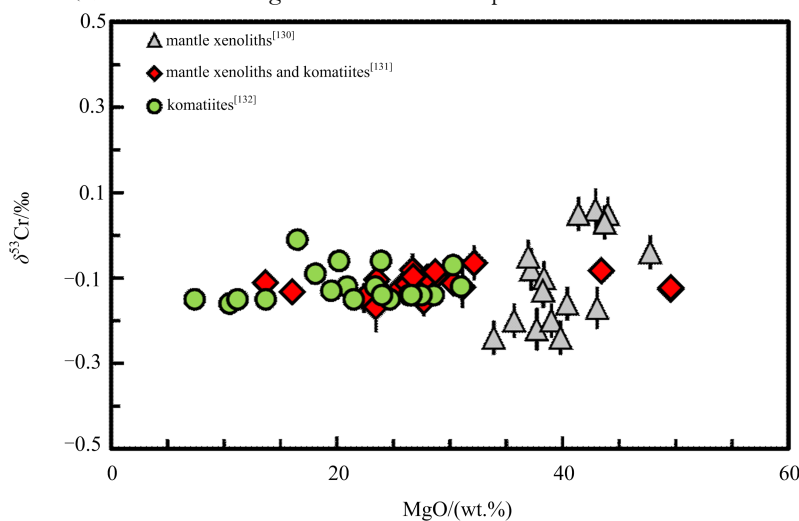
$-0.17 \pm 0.06\%$ (2SD) to $-0.07 \pm 0.04\%$ (2SD), with an average of $-0.11 \pm 0.05\%$ (Fig. 2). A most recent work by Jerram et al.^[132] presented that Cr isotope compositions of a series of the komatiites formed from 2.7 billion years(Ga) to 89 million years (Ma) are relatively constant, and have a limited range of $-0.16 \pm 0.02\%$ (2SD) to $-0.01 \pm 0.02\%$ (2SD). These komatiites have an average value of $-0.12 \pm 0.04\%$, which is consistent with previous studies (Fig. 2). In summary, the average Cr isotope composition of the earth mantle and the bulk silicate earth are most likely in a range of -0.14% to -0.11% .

1.1.2 Partial melting process

In the studies by Schoenberg et al.^[129] and Xia et al.^[130], refractory peridotites tend to be enriched in heavier Cr isotope compositions than fertile ones, indicating Cr isotope could be fractionated during the partial melting process. Xia et al.^[130] speculated that the isotope fractionation might be in relation to the isotopically heavier residual mineral (e. g., spinel) relative to melts. This speculation was based on the previous two works. First, Farkaš et al.^[133] conducted stable Cr isotope analyses of globally distributed 30 mantle-derived chromites, which display a slightly heavier Cr isotope composition (with an average $\delta^{53}\text{Cr}$

value of $-0.08 \pm 0.13\%$) than the average value of the BSE. Subsequently, Shen et al.^[134] also obtained that chromite-bearing peridotites have heavier Cr isotope compositions than adjacent chromite-free ones. However, the partial melting process of mantle peridotites involved consumption of some mantle minerals and generations of melts and many mantle minerals.

To fully understand the Cr isotope fractionation behavior and mechanism, Shen et al.^[75] focused on mantle minerals (olivine, pyroxene and spinel) from mantle peridotite xenoliths (including lherzolites, clinopyroxene-rich lherzolites, and wehrlites) in the Cenozoic basalts from the North China Craton. Two methods have been used to approach the equilibrium inter-mineral Cr isotope fractionation factor, as well as influences from mineral structures and redox conditions. Firstly, Shen et al.^[75] conducted the synchrotron radiation X-ray near-edge absorption spectroscopy (XANES) analyses to quantitatively determine ratios of $\text{Cr}^{2+}/\text{Cr}^{3+}$ in olivines, pyroxenes and spinels, and obtained approximately 20% Cr^{2+} in the olivine from lherzolites and clinopyroxene-rich lherzolites, while the Cr in olivines from wehrlites is basically +3, implying incorporations of the subducted oxidizing material



Data from Refs. [130-132]. Data of samples, that were proposed to have suffered significantly from metasomatism, have been excluded. The compilation indicates the partial melting process could lead to Cr isotope fractionation, generating isotopically lighter melts.

Fig. 2 Compilation of Cr isotope compositions of mantle xenoliths and komatiites

(e. g., sedimentary carbonate) in the Pacific slab oxidized Cr^{2+} to Cr^{3+} . Cr^{2+} is not found in orthopyroxene, clinopyroxene and spinel in all samples, which is in line with previous experimental data and observation results of lunar basalt pyroxene, indicating that Cr^{2+} in pyroxene was oxidized by Fe^{3+} and Ti^{4+} during the cooling process^[6]. Combining the mineral crystal structure model and the basic theory of isotope, the equilibrium fractionation coefficient between the mineral phases, generally follows the order of $\text{Spl} > \text{Cpx}$, $\text{Opx} > \text{Ol}$. Secondly, the analysis results of individual minerals from the lherzolites show that these minerals have reached the equilibrium of Cr isotope fractionation, and the fractionation factors are consistent with the calculation results of the model^[75]. Using inter-mineral equilibrium fractionation factors, the isotope composition feature of part of reported mantle xenoliths could be interpreted by the isotope fractionation during partial melting^[75]. Recently, Bonnand et al.^[76] conducted dissolution and crystallization experiments of chromites from basaltic magmas and obtained that, in both cases, melts were isotopically lighter than equalized chromites, consistent with the result from Ref. [75].

1.2 The earth core and chondrites

Metal-silicate segregation is one of the most important differentiation events in the early solar system^[15]. For terrestrial planets and differentiated asteroids, a metallic inner core and a silicate outer mantle formed after this event. The chemical signatures of the mantle were dramatically changed from the chondritic compositions, especially for siderophile elements. Considering the different bonding environments and valence states of siderophile elements between metal and silicate, isotopic signatures of these siderophile elements in the mantles or cores may also be changed from the bulk planets. The magnitude of fractionation is dependent on the core formation conditions.

For the Earth, the Moon, and some asteroids, mantles are depleted in Cr, which is likely to result from core formation^[20, 135]. Chromium is increasingly siderophile under higher temperature, more reduced conditions, or with elevated S and C contents in the metal^[136]. Compared with the Cr element system, Cr isotope could help to provide further constraints on the core formation conditions, and to shed light on the nature of Cr depletion in the terrestrial and lunar mantle. A series of Cr isotope studies on different planetary reservoirs^[15, 129-132, 137, 138], as well as the Cr isotope fractionation factor determination between metal and silicate in high temperature-pressure metal-silicate experiments^[137, 139] have been conducted.

High temperature-pressure experiments conducted showed no significant Cr isotope fractionation between molten metal and silicate melt at 1.5 GPa and 1923 K, but their experiments suffered from the loss of Cr to the capsules, indicating the system was not in equilibrium^[137]. Subsequent systematic high temperature-pressure experiments overcame the problem of Bonnand et al.^[137] and showed that the heavier Cr isotopes were preferentially enriched in the metal phases relative to the coexisting silicate phases, with $\Delta^{53}\text{Cr}_{\text{metal-silicate}}$ of $0.08 \pm 0.01\%$ at 1873 K, 1 GPa and 6 wt. % Ni content in the metal^[139].

Moynier et al.^[15] reported a lighter Cr isotope composition for all subgroups of chondrites with $\delta^{53}\text{Cr}$ values of -0.2% to -0.4% , which is 0.1% to 0.2% lighter than the bulk silicate Earth (BSE). The heavier Cr isotope composition of the BSE was suggested to have resulted from light Cr isotope entering the metal phase preferentially during core formation, and a relatively low core formation temperature and highly oxidizing conditions were needed to induce such a large isotope variation between chondrites and the BSE^[15]. However, subsequent Cr isotope measurements on chondrites showed no resolvable difference^[129, 131, 132, 137, 138], which is consistent

with the high temperature condition (>3000 K) of terrestrial core formations and experimental results^[139]. The $\delta^{53}\text{Cr}$ values of the lunar mantle and the Vesta's mantle were constrained to be $-0.21 \pm 0.06\%$ and $-0.22 \pm 0.03\%$, respectively^[131, 137, 140], which is $\sim 0.1\%$ lower than the chondritic value. The core formation temperature of these small planets is relatively low, so the core formation effect on Cr isotopic compositions of mantles is larger for the Moon and Vesta. If core formation occurred under a relatively reduced condition or elevated S and C contents in the core, the core formation process could totally or partially account for the lighter-than-chondrites Cr isotope compositions of mantles of the Moon and Vesta. Iron meteorites have extremely heavy Cr isotopic composition ($\delta^{53}\text{Cr}$ value up to 2.85%), and this signature cannot be the result of asteroidal core formation and possibly reflect the effect of fractional crystallization^[141].

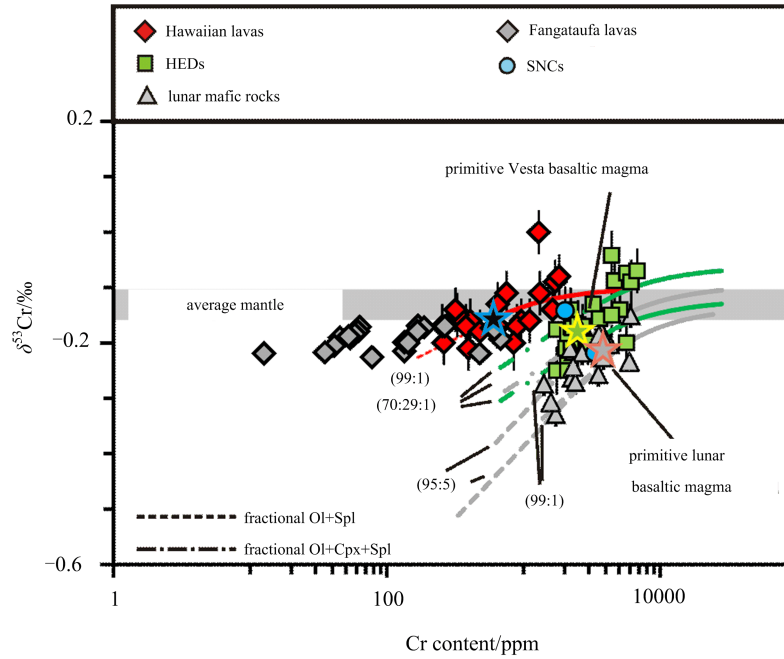
1.3 The igneous crust and fractional crystallization processes

Having resolved isotope fractionation behaviors during partial melting processes, mafic magmatic evolution is also proposed to be capable of causing Cr isotope fractionations. Bonnand et al.^[142] first systematically investigated lunar mare basalts represented by mafic rocks from the Apollo mission. They obtained that the $\delta^{53}\text{Cr}$ values for lunar mare basalts were positively correlated with indices of magmatic differentiation, such as Mg# and Cr contents, reflecting Cr isotopes were fractionated during the lunar mafic magmatic differentiation. They speculated that spinel and pyroxene were the main phases controlling the Cr isotope composition during fractional crystallization, due to ① equilibrium fractionation where heavy isotopes are preferentially incorporated into the spinel lattice, or ② a difference in isotope composition between Cr^{2+} and Cr^{3+} in the melt. This was subsequently documented by Shen et al.^[75]. Additionally, Shen et al.^[75] also speculated that the low oxygen fugacity environment tends to

induce larger isotope fractionation during the fractional crystallization and partial melting. Thus, considering that terrestrial basalts ($\sim\text{FMQ}$) are often more oxidized than the lunar basalts (IW to IW-2), the question of whether isotope fractionations could or not occur during fractional crystallizations of terrestrial basalts remains unconstrained.

Both Shen et al.^[143] and Bonnand et al.^[144] have conducted Cr isotope composition analyses of oceanic island basalts (OIB) from Hawaii and Fangataufa Island, respectively. The consistent observation displayed that via the progressive fractional crystallization, residual melts became isotopically lighter, while accumulates had heavier Cr isotope compositions. The Cr isotope fractionation during the fractional crystallization was attributed to spinel/chromite and clinopyroxene fractional crystallization and accumulation (Fig. 3)^[143, 144]. Combined with the equilibrium fractionation factor determined by Shen et al.^[75] and the oxygen fugacity of the Hawaiian OIB, Shen et al.^[143] presented a fractional crystallization model, which fits the Hawaii OIB data well. Both works gave estimation of Cr isotope compositions of initial OIB magma, ranging from -0.15% to -0.18% (Fig. 3). This value was slightly lighter than the isotope composition of the pristine mantle xenoliths, supporting that partial melting of the mantle peridotites generated isotopically heavier refractory, releasing melts with lighter isotope compositions than the mantle^[130].

So far, there remains a debate for interpretations of the Cr isotope compositions for the lunar and the Vesta mantle. Sossi et al.^[131] analyzed additional lunar igneous rocks based on the lunar marine basalts from Bonnand et al.^[142], and obtained similarly lighter than the BSE isotope composition for the lunar samples. They speculated that the lunar mantle might have a lighter Cr isotope composition than the Earth's mantle, and proposed a volatile loss model during



The stars in different colors are the estimated compositions of initial basaltic melts for Earth, Moon and Vesta. The dotted lines represent fractionation curves for residual melts after fractional crystallization of different mineral assemblages, while the numbers in parentheses are the volumetric proportions of crystallized mineral assemblages, e. g., 99:1 represents fractional crystallization of 99% olivine + 1% spinel by volume, and 90:9:1 represents fractional crystallization of 90% olivine + 9% clinopyroxene + 1% spinel by volume. The solid red and grey lines represent the mixing curves between initial melts and crystallized mineral assemblages (99% olivine + 1% spinel by volume) for terrestrial and lunar cumulates, and the green solid line is calculated by mixing the estimated initial melt for five eucrites and the average composition of two diogenites. The gray area represents the estimated average value of the BSE^[125, 129-132]. Data from Refs. [131, 140-143].

Fig. 3 Compilation of Cr isotope compositions in different terrestrial and extraterrestrial mafic rocks.

The modelling curves for fractional crystallizations and accumulations follow Ref. [143]

cooling and accretion of the Moon. A similar speculation has been made by Zhu et al.^[140], who also found the HED meteorolites from Vesta with a lighter Cr isotope composition than the BSE. However, volatile components of metals as Cr^{0+} were theoretically enriched in light Cr isotopes, which were inconsistent with the isotopically lighter lunar basalts. Both Sossi et al.^[131] and Zhu et al.^[140] proposed that the volatile Cr was in CrO_2 species. A subsequent experiment by Sossi et al.^[145] documented Cr volatilizations might lead to Cr isotope fractionation generating lighter isotopically melts. The other argument is that the lunar mantle and the Vesta mantle have indistinguishable Cr isotope compositions from the earth mantle (Fig. 3)^[75, 142-144]. We speculated that the obtained isotope composition differences among the earth terrestrial basalts, and lunar and Vesta basalts might be a result of partial melting and

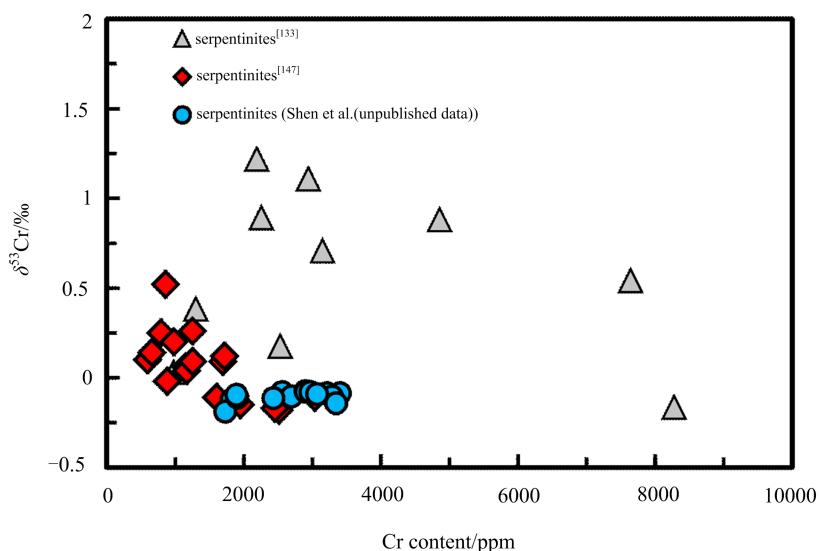
fractional crystallization under different oxygen fugacity environments^[143]. Combined with the previous published data, we present a quantitative model that relates the Cr isotope compositions of basalts from the Earth, the Moon and Vesta to the crystallization assemblage, the degree of fractional crystallization and the $\text{Cr}^{2+}/\Sigma\text{Cr}$ ratios of minerals and melts, which are related to the different oxygen fugacity environments for different planets. The initial lunar mantle is estimated to be relatively homogeneous, with a BSE-like Cr isotope composition (-0.16‰ to -0.09‰ , Fig. 3). Further work is needed in the future to test the detailed effects of these two processes on Cr isotope systems for planetary formation and evolution.

1.4 Serpentinization and high temperature-pressure metamorphism

Serpentinization is the middle-low temperature ($< 500\text{ °C}$) hydrothermal alteration of mafic and

ultra-mafic rocks in the surface and near-surface environments, mainly occurring in the ocean floor, mid-ocean ridges, and subduction zones^[146]. Farkaš et al.^[133] first found that along with increased degree of serpentinizations, Cr isotope compositions of serpentinites tend to incorporate heavier Cr isotopes (up to +1.22‰, Fig. 4). They have interpreted it as a result of a large amount of Cr³⁺ being reduced from isotopically heavy Cr⁶⁺ components in the hydrothermal fluid by Fe²⁺ or H₂, which were produced during the serpentinization process. This explanation requires that the hydrothermal fluid have high Cr contents and heavy Cr isotope compositions. However, with respect to common hydrothermal fluids, such as low-temperature hydrothermal fluids (seawater), the Cr content is much lower than peridotite (about 0.05~1 ppb), and the Cr isotope composition is about +0.41‰ to +1.51‰^[41, 45]. Although the Cr content in magma hydrothermal fluids is relatively high (such as ultramafic and mafic magmas, up to thousands and hundreds of ppm, respectively), Cr mainly exists in the form of +3, and the Cr isotope composition is close to the BSE. Obviously, seawater and magmatic hydrothermal fluids cannot explain the observed serpentinite data. Subsequently, Wang et al.^[147]

conducted systematic comprehensive analyses of the three holes of the Global Ocean Deep Sea Drilling Program (ODP) 897C, 897D, and 1070A, the ophiolites from Northern Apennines in Italy, and the serpentinites in the Syros subduction zone complex. These serpentinites also display a large isotope variation range (-0.2‰ ~ +0.6‰, Fig. 4). Compared with the work by Farkaš et al.^[133], Wang et al.^[147] also observed a roughly negative correlation between $\delta^{53}\text{Cr}$ and Cr contents in serpentinites, and proposed two possible explanations: ① During serpentinization, partial Cr³⁺ was oxidized to Cr⁶⁺, which is enriched in lighter Cr isotope compositions due to kinetic fractionations; ② A multi-stage alteration process was proposed, including the oxidation of Cr³⁺ in the peridotite in the early serpentinization process, forming a Cr⁶⁺-bearing fluid with the BSE-like isotope composition. Via the long-term water-rock interaction, the Cr³⁺ in serpentinites and the Cr⁶⁺ in fluids reach the isotope fractionation equilibrium, which causes serpentinites to be enriched with light Cr isotopes, while the fluid is enriched with heavy Cr isotopes. Finally, part of the Cr⁶⁺ with heavy Cr isotopes in fluids re-enters the serpentinites by sulfide reduction. For the first possibility, there is currently a lack of relevant



Data from Farkaš et al.^[133], Wang et al.^[147], and Shen et al. (unpublished data).

Fig. 4 Whole-rock Cr contents versus Cr isotope composition diagram in serpentinites from different areas

experimental evidence. The latter possibility is more complicated. Although its feasibility cannot be judged, it also needs to face the problem of mass balance, that is, how much Cr^{6+} in the reducing fluid is efficient to change Cr isotope compositions of ultramafic rocks. Recently, we have conducted Cr isotope composition analyses of serpentinites in different tectonic settings from Tonga, Xigatse, western Tianshan, and Cyprus (Shen et al., under review^①; Shen et al., unpublished data^②). Our data displayed that Cr isotope fractionation behaviors during serpentinizations were complex, which was dependent on mineral-water interactions and unique tectonic setting environments. Therefore, there is still a lot of controversy over the mechanism of Cr isotope behaviors during serpentinization, and further research is required.

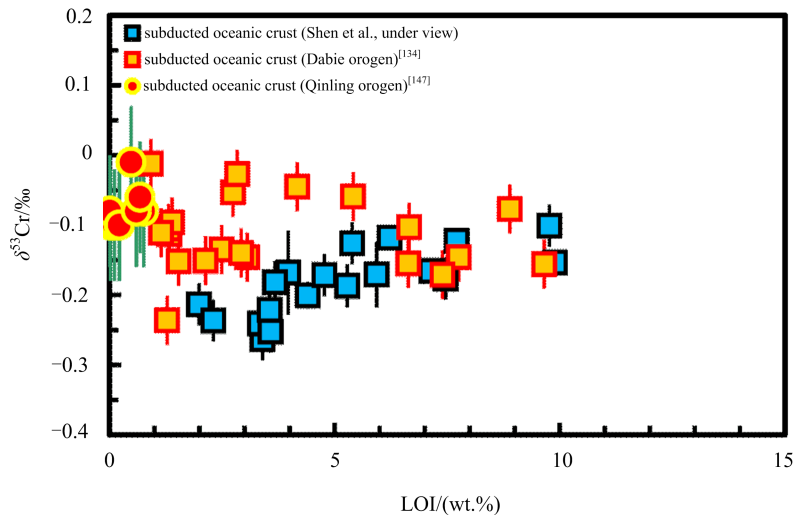
Recent experimental and natural observations have highlighted a significant enhancement of Cr mobility with increased Cl^- contents and reduced environments in fluids under lower crust and upper mantle P-T conditions^[148-154]. Abundant Cl^- released during serpentinite dehydrations (0.3 wt. % to 2.56 wt. % in fluids)^[155] should have the capacity to transfer Cr^{3+} from serpentinites into subduction fluids, which might modify the subduction zone complex and overlying mantle wedge, as well as potential arc lavas. So far, no direct observations on Cr isotope fractionation during serpentinite dehydrations have been reported, and more work is expected in future.

Schoenberg et al.^[125] tested some metamorphic minerals (including fuchsite and uvarovite), which have heavier Cr isotopic composition of $-0.05\text{‰} \sim 0.05\text{‰}$, but there is no clear explanation. Farkaš et al.^[133] also evaluated the behavior of Cr isotopes in many metamorphic processes (such as hydration, carbonatization, low-high temperature metamorphism, and so on). The analyzed minerals were crocoite, fuchsite, stichtite, serpentine, chrome pyrope, chrome chalcidony, chrome diopside and chrome tremolite. All these

minerals have heavier Cr isotope composition than the BSE and the mantle-derived chromites, implying that metamorphisms might cause the minerals to become isotopically heavier. Subsequently, Shen et al.^[134] and Wang et al.^[147] have analyzed whole-rock Cr isotope compositions of the metamorphic mafic rocks with varying metamorphic degrees from Dabie-Sulu orogen, eastern China, to investigate the Cr isotope behavior during the continental crust subduction. The greenschists, amphibolites and eclogites display the BSE-like Cr isotope composition features. Lack of resolvable isotope variability among the metamorphic rocks from different metamorphic zones might indicate that no systematic Cr isotope fractionation was associated with the degree of metamorphism (Fig. 5). Furthermore, Cr isotope was also fractionated limitedly during retrograde metamorphisms based on the eclogite-amphibolite lenses from Shuanghe^[134]. One possible explanation might be a lack of fluid or a Cr-poor fluid from subducted sediments during the continental crust subduction, which hinders Cr mobility and thus limits Cr isotopic fractionation^[134]. Compared with the continental crust subduction settings, the subduction of the oceanic crust, which contains amounts of hydrous Cr-rich reservoirs (especially serpentinites, alteration oceanic mafic rocks), might provide diverse constraints on the Cr isotope system in the subduction zone (Fig. 5). For example, Shen et al. (under review) has obtained that the eclogites and blueschists from western Tianshan recorded dehydrations of serpentinites in the oceanic subduction channel (Fig. 5). This work might give rise to more attention on using Cr

① SHEN J, WANG SJ, QIN LP, et al. Tracing serpentinite dehydration in a subduction channel: Chromium isotope evidence from subducted oceanic crust. *Geochim Cosmochim Acta*, under review.

② SHEN J, QIN LP, CHEN YX, et al. Chromium isotope systems of serpentinites, implication for Cr recycling in the Earth surface. Unpublished data.



Data from Shen et al. [134], Wang et al. [147], and Shen et al. (under view).

Fig. 5 Whole-rock LOI versus Cr isotope composition diagram of metamorphic mafic rocks from subducted oceanic crust (Southwestern Tianshan) and continental crust (Dabie orogen and Qinling orogen)

isotopes as a potential index for serpentinite-derived fluids in subduction zones.

As previously discussed, since the mantle hosts most Cr and has high Cr contents, the effects of mantle metasomatism on Cr isotope compositions were generally considered to be limited. At the mineral-scale, Shen et al. [75] found that metasomatism could influence Cr isotope compositions of minerals from Beiyuan metasomatized clinopyroxene- (Cpx-) rich lherzolites and wehrlites by means of mineral-melt interaction and/or kinetic diffusion, leading to disequilibrium inter-mineral Cr isotope fractionation. Especially, during metasomatism, Cr isotope compositions of spinels were relatively constant, while Cr isotopes of olivine and pyroxenes were more variable [75]. Chen et al. [156] also obtained that olivine and pyroxenes were Cr isotopically heavier than co-existing chromites in Kizildag ophiolites, attributing to metasomatism and partial melting or fractional crystallization. At the whole rock-scale, Xia et al. [130] obtained two pyroxenite veins from Shavaryn displaying very light Cr isotope compositions of $-1.36 \pm 0.04\%$ and $-0.77 \pm 0.04\%$ with complementary isotopically heavier lherzolites, which has been interpreted as a result of kinetic diffusions during

the melt infiltration and metasomatism. Therefore, the high temperature metamorphism and metasomatism in the mantle are capable of modifying the Cr isotope composition of the mantle xenoliths by interactions between rock (mineral) and melt or kinetic diffusions.

A recent work by Bai et al. [157] combined the Cr elemental zoning and Cr isotope compositions in mineral separates, and highlighted a new potential implication of the Cr isotope system for assessing time scales of magma cooling, based on the well constrained Cr diffusion behavior in spinel, olivine and orthopyroxene [158-160]. Although this method is original, further tests are required to verify this hypothesis.

2 Conclusion

In the last decade, the chromium isotope system in high-temperature settings has achieved plenty of remarkable results. This paper has reviewed most of the works recently reported in this area to evaluate current Cr isotope research status, as well as the remaining problems. In the following, we will list and highlight the potential research directions and hot points in the future:

(I) Chromium isotope compositions of upper crust remain unconstrained, which is an important

reservoir of the crust.

(II) Mechanisms and controlling factors for Cr isotope fractionations during serpentinizations should be constrained. Cr isotope behaviors during weathering of serpentinites and subduction dehydration of serpentinites also need assessments, which influence reconstructions of the ancient oxygen level and crust-mantle Cr isotope recycling, respectively.

(III) More high temperature-pressure experiments on Cr isotope fractionations for core-mantle differentiation are needed to further constrain physical and chemical conditions for planetary evolutions.

(IV) More work is also expected focusing on Cr valences and Cr isotope fractionations of rocks from different planetary bodies to assess attributions from volatilizations and inter-planetary differentiations to their Cr isotope compositions.

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