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Gondwana Research 12 (2007) 67–76
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Chondritic osmium isotopic composition of Archean ophiolitic mantle, North China craton

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Received 12 December 2005; received in revised form 20 October 2006; accepted 26 October 2006
Available online 29 December 2006

Abstract

Podiform chromitites are diagnostic but rare features of Phanerozoic ophiolites, and often contain the most pristine textural, chemical and isotopic record of convective upper mantle conditions extant during ophiolite genesis. Ophiolitic podiform chromitites, owing to their high Os concentrations and low Re/Os ratios provide the best evidence for the Os-isotopic evolution of oceanic mantle, but established records of ophiolitic chromites from bona fide Archean ophiolites are still lacking. We report Re–Os isotopic compositions of the world's oldest known ophiolitic podiform chromites from the 2.5 billion year old Dongwanzi–Zunhua ophiolite, North China. This provides the oldest Os isotope composition for the convective upper mantle yet obtained from ophiolitic podiform chromitites, and reveals a chondritic Os isotopic composition of the Archean convective upper mantle.

Keywords: Re–Os; Archean ophiolite; Chromitite; Chondritic; Convective upper mantle

1. Introduction

The Re–Os isotopic system provides critical information on the accretion history of the planet, the distributions of highly siderophile elements (HSEs) in Earth's interior, and the differentiation and evolution of the Earth and its components including the core, mantle and crust (Roy-Barman and Allegre, 1994; Snow and Reisberg, 1995; Schiano et al., 1997; Roy-Barman et al., 1998; Shirey and Walker, 1998; Brandon et al., 2001; Meisel et al., 2001). The Os isotopic composition and evolution of the convecting upper mantle are related to partial melting in the mantle and the recycling of crust via subduction. During mantle melting processes, rhenium is a moderately incompatible element whereas osmium is highly compatible. Therefore, mantle-melting processes such as extraction of oceanic crust affect the mass balance of these elements in the residual mantle, leaving rhenium depleted relative to osmium. If subducted slabs of oceanic lithosphere remain geochemically isolated from the convecting upper mantle, then the $^{187}Os/^{188}Os$ ratio of the mantle should grow more slowly with time relative to undepleted mantle. Determining the $^{187}Os/^{188}Os$ of the convective upper mantle has been previously attempted through analysis of abyssal peridotites, Mid-Ocean Ridge Basalts (MORB) and MORB related glasses and sulfides (Roy-Barman and Allegre, 1994; Snow and Reisberg, 1995; Schiano et al., 1997; Roy-Barman et al., 1998; Shirey and Walker, 1998; Brandon et al., 2001; Meisel et al., 2001).

Ophiolites represent slices of oceanic lithospheric crust and mantle thrust onto continental crust. The $^{187}Os/^{188}Os$ ratios of ophiolitic mantle peridotites may reflect the original characteristics of the Os isotopic composition of the convecting upper mantle at the time the ophiolite formed. Podiform chromites are typically found in ultramafic mantle tectonite portions of ophiolites, and most form through crystallization from a partial melt in dunite lenses within mantle or overlying crustal sequences, or as a result of melt–rock or melt–melt interaction

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doi:10.1016/j.gr.2006.10.023

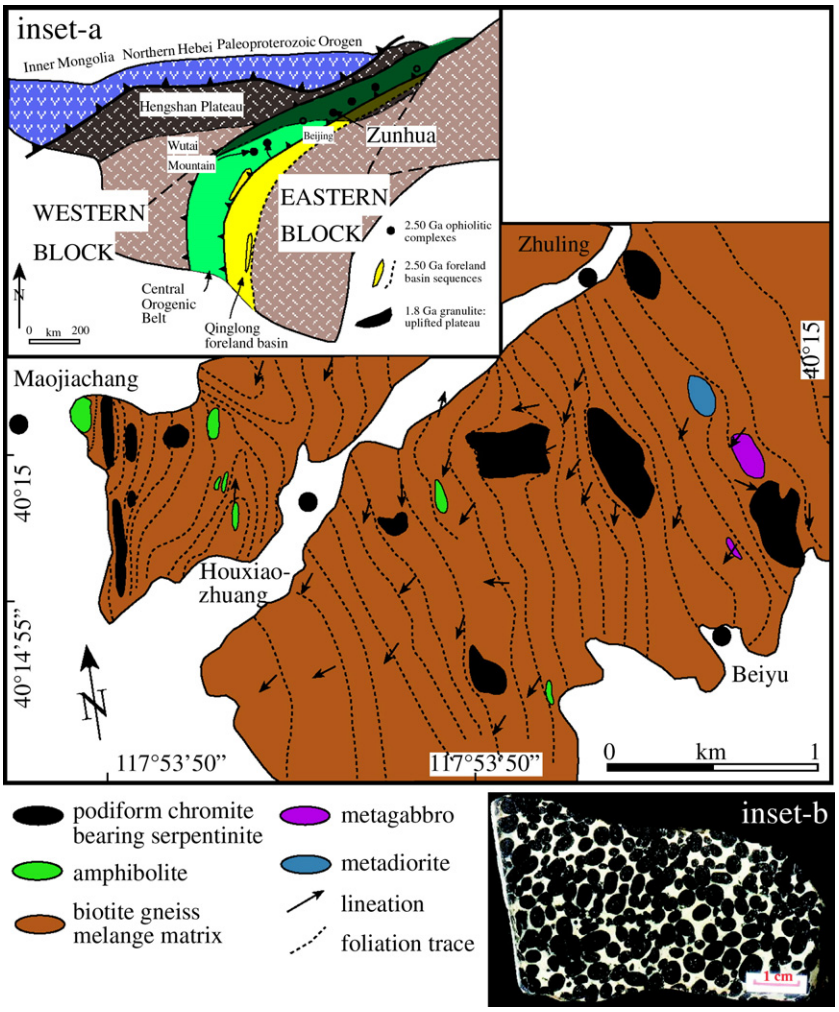

Fig. 1. Geological map of the North Zunhua area showing the distribution of ophiolitic blocks in a biotite- and hornblende-biotite gneiss matrix, based on mapping by authors. Inset-a shows tectonic setting of area in the Archean Central Orogenic belt, an Archean suture between the Eastern and Western blocks of the North China craton. Inset-b is a typical field sample of nodular chromites in serpentinized dunite.

near the crust–mantle boundary (Lago et al., 1982; Nicolas, 1989; Leblanc and Nicolas, 1992; Zhou et al., 1996a,b; Edwards et al., 2000). Because of the high Os concentrations and low Re/Os of podiform chromites, the in situ decay of ^{187}Re into ^{187}Os has minimal impact on ^{187}Os/^{188}Os subsequent to formation. Most mantle tectonite sections of ophiolites are highly serpentinized, from both seafloor alteration and obduction processes. Serpentinization can lead to open-system behavior of the Re–Os system (Snow and Reisberg, 1995). Podiform chromites are extremely resistant to the modification of initial Os isotope compositions through serpentinization or radiogenic fluids or melts derived from subducting slabs.

Ophiolitic chromites of different ages provide the best samples for the study of the long term ^{187}Os/^{188}Os evolution of convecting upper mantle (Walker et al., 2002a,b). Walker et al. (2002a,b) reported Os isotopic compositions of podiform chromites separated from upper mantle and crustal portions of 18 ophiolites from MORB, back arc, and supra subduction zone (SSZ) settings, ranging in age from 50 Ma to 900 Ma. The oldest known ophiolites that Os isotopic compositions have been reported from are the Paleoproterozoic Outokumpu (Walker et al., 1996) and Jourma (Tsuru et al., 2000; Peltonen et al., 2003; Kusky, 2004) ophiolites in eastern and northern Finland and a probable Archean ophiolite from the Ukrainian Shield (Gornostayev et al., 2004). Re–Os system data for chromitites and chromite separates from mafic–ultramafic bodies in the Ukrainian Shield were reported (Gornostayev et al., 2004). But there is no solid and sufficient evidence to conclude that those massifs represent strictly-defined ophiolites of 3.0 Ga. In contrast the formation age of chromitite bearing Lipovenki and Kapitanov massifs within the Golovanevsk suture zone in the Ukrainian shield are constrained by an Os isotope model age based on a chondritic evolution trajectory of Archean convective upper mantle (Gornostayev et al., 2004).

Until recently, these circa 2.0 Ga Paleoproterozoic ophiolites were the oldest recognized on the planet (Kusky et al., 2001; Li et al., 2002; Kusky, 2004); thus, obtaining older oceanic mantle compositions from ophiolitic podiform chromitite was not possible. A complete 2.5 Ga ophiolite has recently been recognized in the Dongwanzi–Zunhua area of the North China craton (Kusky et al., 2001; Li et al., 2002; Kusky, 2004), with dismembered ophiolites distributed in an ophiolitic mélange belt

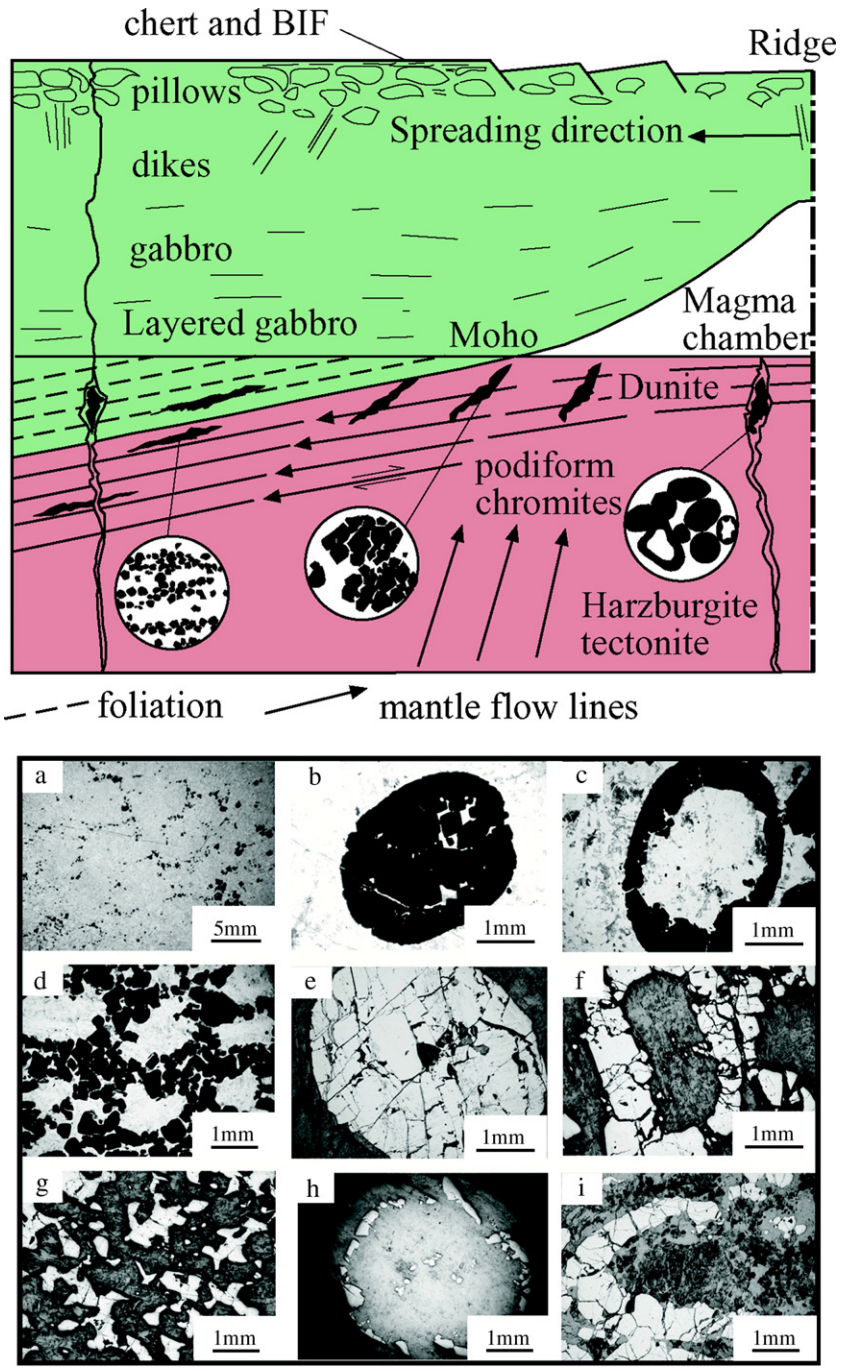

Fig. 2. Model for the formation of podiform chromites within off-axis intrusions into the base of the oceanic lithosphere. a, b, and c show typical fabric development stages as the podiform nodular and orbicular chromites are progressively sheared as the oceanic lithosphere moves away from the ridge axis (Nicolas, 1989; Kusky, 2004). Photomicrographs in lower half of figure show different textures within podiform chromitite. a shows chromite grains (dark) surrounding antinodular texture of serpentinized dunite, b shows chromite nodule in serpentinized dunite matrix, c shows orbicular chromite inside and including serpentinized dunite. d is a well-developed antinodular chromite, e shows silicate inclusions inside (light colored, reflected light) chromite grain, and f shows orbicular chromite (light) in reflected light. g shows interstitial chromite (light) between serpentinized olivine cumulates, h shows incipient orbicular chromite, and i shows broken, magmatically deformed orbicule in reflected light.

exposed for more than 600 km in the Central Orogenic suture belt between the Eastern and Western blocks (Fig. 1) of the craton (Kusky et al., 2001; Li et al., 2002; Kusky, 2004). These dismembered ophiolites contain a small amount of tectonized mantle rocks, but deformation is complex and most original mantle textures and mineral parageneses are overprinted.

Spectacular podiform chromitites are located within tectonic blocks in this ophiolitic mélange belt, and are particularly well-preserved in the Zunhua structural belt (Gornostayev et al., 2004; Polat et al., 2005) (Fig. 2). The 2.5 billion year old Zunhua podiform chromitites preserve delicate magmatic and deformation textures and structures known previously only

from much younger oceanic mantle rocks, and thus preserve a unique remnant of Archean oceanic mantle.

Systematic studies of the components, structure and formation mechanisms of the Zunhua podiform chromitites confirm these are dismembered Archean ophiolites (Kusky, 2004). The Re–Os contents and the Os isotopic compositions of podiform chromitites and chromite separates from Zunhua ophiolites are reported in this study, after an assessment of the structural setting, textures and trace element chemistry, and used as the presently best-known constraint on the Os isotopic composition of Archean convecting upper mantle. This work supersedes earlier Re–Os results reported in Kusky (2004).

2. Geology and petrology

Detailed field and petrographic analysis of mafic to ultramafic blocks in the Zunhua structural belt, North China (Fig. 1) has revealed many different metamorphosed oceanic crust and mantle rock types including serpentinized harzburgite, peridotite tectonite, dunite, podiform chromitite, hornblendite, wehrlite, pyroxenite, gabbro, cumulates, pillow lavas, massive basalt, garnet amphibolite, and greenschist (Fig. 1). The blocks are interpreted as strongly dismembered fragments of an originally more continuous ophiolite sequence (Li et al., 2002; Kusky, 2004), tectonically mixed with Neoarchean biotite- and hornblende-biotite gneiss, amphibolite, and banded iron formation, interpreted as metasedimentary and metavolcanic components of an ophiolitic mélange. All these units are intruded by ca. 2.50–2.40 Ga granite (Li et al., 2000, 2002; Wilde et al., 2002; Kusky and Li, 2003; Polat et al., 2005, 2006) demonstrating their Archean ages.

Gabbro and pyroxenite boudins exhibit well-preserved relict cumulate textures (Li et al., 2002). Serpentinized dunite exhibits well-defined layering defined by needle-like chromite grains. Relict olivine forms extended ribbons with asymmetrical geometry and deformation kink bands (Li et al., 2002). Small amounts of chromite (<5%) are euhedral to subhedral. These fabrics are attributed to mantle flow at high temperatures. Olivine crystals are commonly serpentinized, with magnetite distributed along foliation planes.

Peridotite blocks are composed of serpentinized ribbon-olivine, relict orthopyroxene, chromite, and minor magnetite (Figs. 1b and 2). Stretched orthopyroxene grains form augen up to 2–3 mm in diameter enclosed in a serpentinite matrix, and display ribbon-shaped tails. Some orthopyroxene porphyroclasts preserve embayed outlines associated with corrosion by melt. Minor sub- to euhedral-chromite is present. Metamorphic harzburgite tectonite fabrics are defined by oriented orthopyroxene porphyroclasts, strings of chromite, and elongated ribbons of olivine (Kusky et al., 2001; Li et al., 2002; Gornostayev et al., 2004; Kusky, 2004). These textures form during high-temperature plastic deformation in the mantle (Nicolas and Azri, 1991; Holtzman, 2000). Early high-temperature tectonite fabrics in the peridotite are cut by late steeply dipping serpentinized shear zones oriented parallel to tectonic contacts with country rocks, interpreted as late obduction-related deformation (Li et al., 2002).

Six large and numerous smaller chromite-rich peridotite massifs in the southwestern Zunhua structural belt (Fig. 1) are hosted in dunite envelopes within intensely serpentinized and strongly foliated harzburgite. Serpentinized pods show concentric rings with systematic variations in mineral composition and texture — outer rings are 2–10 cm thick and composed of serpentine, whereas inner cores preserve dunite or massive harzburgite. Narrow deformed pyroxenite dikes (1–10 cm wide) cutting serpentinized harzburgite are interpreted as melt channels or trapped parental melts to oceanic basalt. Magmatic and tectonic fabrics defined by chromite are well preserved in the cores of the serpentinized pods.

Dunite envelopes are common features of podiform chromitites. They are known to form almost exclusively in the mantle or crust–mantle transition zone of suprasubduction zone (harzburgite type) ophiolites of different ages (Nicolas and Azri, 1991; Holtzman, 2000; Li et al., 2002; Kusky, 2004). Most of the chromitites are strongly deformed by plastic flow, although nodular chromitites are locally preserved, especially in discordant pods. Igneous textures including nodular, orbicular, banded, massive, antinodular, and disseminated chromitite varieties are all present (Fig. 2), and in many places grade into each other. Nodular textures consist of small (2–10 mm) balls of chromite in a dunite matrix (Fig. 2), whereas orbicular chromitites consist of thin-rings of chromite surrounding cores of dunite (Fig. 2). Some nodular and orbicular chromites grade into massive chromites, or disseminated grains. Nodular and orbicular textures are the most typical magmatic structures of ophiolitic chromitites (Thayer, 1964; Nicolas and Azri, 1991; Nicolas, 1989; Zhou et al., 1996a,b). In places these magmatic textures show a sequence of progressive deformation into harzburgite-tectonites, with evidence for high-temperature mantle deformation. Pull-apart textures (Fig. 2) characteristic of deformation at greater than 1200 °C (Holtzman, 2000) are common in the massive chromitite deposits. Abundant deformed olivine, orthopyroxene, and other silicates occur as inclusions in the chromitite, indicating that the chromite bearing melts flowed through and included xenocrysts of previously deformed harzburgitic mantle (Li et al., 2002). Orthopyroxene porphyroclasts in the matrix show asymmetrical recrystallized tails indicating high-temperature shearing after the podiform chromites were crystallized at the base of the Archean oceanic lithosphere.

The sample localities in this study include the Maojiachang, Zhuling, Lvshigou, blocks in the Zunhua map area (Fig. 1). For chemical and isotopic analyses, we sampled the most pristine chromitites, preserving igneous textures. Altered ferritchromites were carefully avoided.

Chromite can be used as a petrogenetic indicator to help constrain the tectonic affinity of ultramafic massifs (Thayer, 1964; Edwards et al., 2000). Chromite from the ultramafic fragments in the Zunhua mélange beneath the Dongwanzi ophiolite has a very refractory composition, with high Cr and low Ti, Cr_2O_3 contents larger than 50%, and $Cr^{\#}$s Cr/(Cr+Al) of 0.74 to 0.93, TiO_2 at less than 0.3 wt.%, and V_2O_5 wt.% at less than 0.1 (Kusky, 2004). Disseminated chromite has lower $Cr^{\#}$ higher V_2O_5 contents than the nodular and orbicular varieties.

The Fe_2O_3 wt.% is variable, with a range from 3.2–13.2. Higher Fe_2O_3 content in some samples is attributed to alteration from chromite to ferrite-chromite (Kusky, 2004). In diagrams of TiO_2 versus Cr_2O_3, the Zunhua chromitites all plot within the ophiolitic field (Kusky, 2004). Chondrite-normalized platinum group elements (PGE in order of Os, Ir, Ru, Rh, Pt, Pd and Au) distributions of the Zunhua chromitites display evident negative slopes, similar to those of the Oman, Greece and Dongqiao and Luobusa ophiolites, Tibet (Lago et al., 1982; Nicolas, 1989; Leblanc and Nicolas, 1992; Zhou et al., 1996a,b; Edwards et al., 2000). The mineral chemistry of the Zunhua chromitites suggests that they formed in a suprasubduction zone ophiolitic environment (Kusky, 2004). The $Cr^{\#}$, TiO_2 wt.% and V_2O_5 wt.% indicate partial melting of a depleted source under high fO_2 conditions. These compositions indicate formation in a SSZ setting and fluid aided melting of a previously depleted source.

3. Re–Os analytical methods

The Re and Os abundances and Os isotopic compositions of the chromite separates, whole rock chromitites and mantle tectonites from the ophiolitic mélange were analyzed at the Department of Terrestrial Magnetism (DTM), Carnegie Institution of Washington, USA and at the School of Earth and Space Sciences, University of Science and Technology of China respectively.

At the Carnegie Institution, the chromites in study (Table 1) were separated and concentrated from samples crushed and grounded to under 250 μm in size, using a Frantz magnetic separator. Re–Os analytical procedures followed the Department of Terrestrial Magnetism protocol, detailed in (Carlson et al., 1999), which includes Carius tube sample digestion and isotopic composition equilibration between sample and spike, CCl_4–HBr extraction and micro-distillation purification of osmium and anion exchange separation and purification of rhenium.

200 mg of the finely ground sample powder were dissolved and equilibrated with spikes Re–Os-99-4-50 with reverse aqua regia in Carius tubes (Shirey and Walker, 1995). The tubes were heated to 220 °C for 15 h. After cooling and uncapping, CCl_4 was added in for the extracting the Os from the solution. Then Os was oxidized by a concentrated CrO_3 solution and extracted into liquid Br_2 (Birck et al., 1997) and finally purified by micro-distillation (Birck et al., 1997). After 3 h, the Os had been distilled and purified.

The isotopic compositions of Re and Os of chromite separates from samples (Table 1) were measured as negative ions using 15-inch mass spectrometry in the DTM lab in Washington, DC. Re and Os were load onto Pt filaments with $Ba(NO_3)_2$ as an activator. Total procedural blanks did not exceed 2.0 pg for both Os and Re. Analytical uncertainty for $^{187}Os/^{188}Os$ is less than ±0.2%.

Re–Os isotopic analysis of whole rock powder made from podiform chromitite samples were carried out on a separate suite of samples (Table 1) in Re–Os laboratory of School of Earth and Space Sciences at University of Science and Technology of China (USTC; for detailed methods see previous reports (Jin et al., 2004; Meng et al., 2004)). About 2 g of finely ground bulk rock power, Re and Os spikes and reverse aqua regia were introduced into a Carius tube (Shirey and Walker, 1995), then heated to 230 °C for a minimum 18 h. The tube was shaken in an ultrasonic vibrator for at least 10 min then heated to 230 °C for a minimum of 18 h again. Os was extracted from the solution via mini distillation (Nägler and Frei, 1997). Final purification of Os was accomplished via micro-distillation (Birck et al., 1997). The Os isotopic compositions were measured using negative thermal ionization mass spectrometry (NTIMS) at USTC (Creaser et al., 1991; Walczyk et al., 1991). Os analyses were made in static mode using six Faraday cups or in peak jumping mode using an electron multiplier on MAT262 mass spectrometer respectively, depending on the signal intensities of OsO_3^- ions of various mass numbers. The measured Os results were corrected for mass fractionation and oxygen isotopic compositions (Zheng et al., 2004). The extraction and purification of rhenium was

Table 1
Re–Os data of Zunhua whole-rock podiform chromitites and chromite separates from the North China Craton

Sample	Rock type	Re (ppb)	Os (ppb)	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$	T_{RD} (Ga)[1]	T_{MA} (Ga)[1]	T_{RD} (Ga)[2]	T_{MA} (Ga)[2]
O1-10-30	Nodular chromite	0.103	35.41	0.014	0.11202	2.38	2.45	2.2	2.27
O1-10-40	Chromite	0.067	34.81	0.009	0.11016	2.62	2.68	2.46	2.52
NC-6	Antinodular chromite	0.052	23.6	0.011	0.11161	2.43	2.49	2.26	2.32
NC-20	Antinodular chromite with envelope	0.033	39.5	0.009	0.11052	2.58	2.63	2.41	2.47
Tk-NCD-01-33a	Disseminated chromite	0.025	5.202	0.023	0.11131	2.47	2.61	2.3	2.43
Tk-NCD-01-33b	Banded chromite	0.034	23.71	0.007	0.11	2.65	2.69	2.49	2.53
O1-10-16	Chromite	0.079	36.09	0.011	0.11122	2.48	2.54	2.31	2.37
NC-13-1	Chromite	0.087	40.08	0.011	0.10969	2.69	2.75	2.53	2.6
NC-19-4	Nodular chromite	0.178	43.84	0.02	0.11068	2.56	2.67	2.39	2.51
Z-3	Folded chromite	0.174	28.62	0.029	0.11058	2.57	2.75	2.4	2.59
D1552	Chromite bearing peridotite	0.02	8.828	0.011	0.11145	2.45	2.51	2.28	2.34
D1577	Chromite bearing peridotite	0.019	31.26	0.003	0.11003	2.64	2.66	2.48	2.5
D1579	Chromite bearing peridotite	0.035	47.43	0.004	0.11006	2.64	2.66	2.48	2.5
D2543-2	Chromite bearing peridotite	0.06	24.01	0.012	0.1111	2.5	2.57	2.33	2.4
D2542	Massive chromitite	0.046	326.9	0.001	0.11027	2.61	2.61	2.45	2.45
D2543-1′	Massive chromitite	0.128	354	0.002	0.11021	2.62	2.63	2.46	2.47
LWH	Massive chromitite	0.049	315.7	0.001	0.1103	2.61	2.61	2.44	2.45

[1] Model 1, with modern Os isotope composition of 0.1296 for enstatite and ordinary chondrites.
[2] Model 2, with modern Os isotope composition of 0.1270 for carbonaceous chondrite.

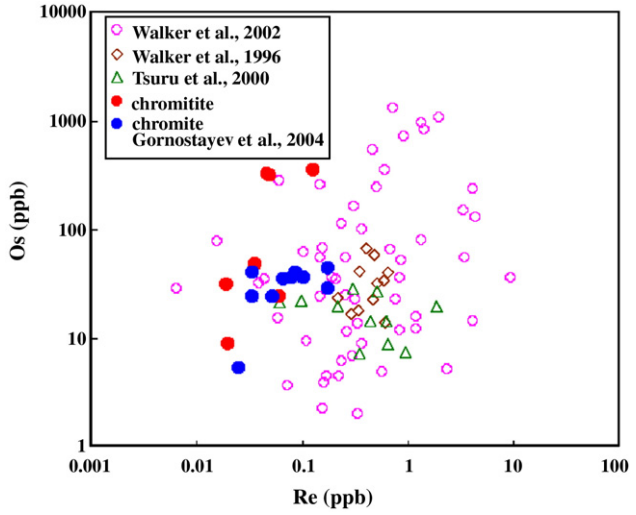

Fig. 3. Distribution of Re and Os contents in ophiolitic podiform chromitites and chromite separates.

completed by AG1X8 anion exchange column. Re isotopic compositions were measured on Finigin MAT Element II ICP-MS in the Department of Earth Science of Nanjing University, China. The precision of $^{185}Re/^{187}Re$ ratios is about 1%. The precision of $^{187}Os/^{188}Os$ ratios is better than 0.04%. $^{187}Os/^{188}Os$ ratio of our lab liquid and lherzolite standards were reproducible within 0.4% (0.17380±0.00064, 1σ, 31 analyses) and 0.7% (0.12266±0.00084, 1σ, 6 analyses) respectively over the course of this study. Total analytical blanks are 2 pg for Re and 5 pg for Os respectively. The $^{187}Os/^{188}Os$ ratio of Os blank is 0.17. The $^{187}Re/^{185}Re$ is common for Re blank. All data were blank corrected.

4. Results

The abundances of Re and Os and $^{187}Os/^{188}Os$ isotopic compositions for Zunhua ophiolitic podiform chromitites and chromite separates from different samples measured respectively at both American and Chinese laboratories are listed in Table 1. The Os concentrations range from 5.20 to 354 ppb while Re concentrations vary from 0.019 to 0.178 ppb. The range of Os concentrations of the samples in this study are similar to those reported for chromites separated from ophiolitic podiform chromitites worldwide in various ages (Walker et al., 1996; Tsuru et al., 2000; Walker et al., 2002a,b; Gornostayev et al., 2004) but the Re concentrations are in the lower range of those reported (Fig. 3). Of the sample set in this study three massive chromitites have much higher Os concentrations averaging of 332±20 (2σ) ppb than that of the rest chromitites and chromite separates, which all are below to 100 ppb (Fig. 3). But the Re concentrations of 3 massive chromitites have no obviously difference with others (Fig. 3). A disseminated chromite has the lowest Re and Osmium concentrations of 0.0247 ppb and 5.2018 ppb respectively in the sample set (Table 1).

The $^{187}Os/^{188}Os$ from ophiolitic chromitites and chromite separates ranges from 0.10969 to 0.11202 averaging of 0.11066± 0.0006 (2σ). The relative variation (0.5%) of measured $^{187}Os/^{188}Os$ in this sample set is rather small and almost similar to the reproducibility of measurement of our USTC Lab liquid and lherzolite standards. The $^{187}Re/^{188}Os$ of the sample set ranges from 0.0007 to 0.0292, much less than the chondritic average of approximately 0.4 (Wang et al., 1995). This low ratio means that there is minimal age correction for most samples, even if quite old. Fig. 4 presents characteristic features of Re–Os isotopic compositions of Zunhua ophiolitic chromitite and chromite separates from both laboratories. A 2.6 Ga chondritic reference isochron with initial $^{187}Os/^{188}Os$ of 0.1100 is also plotted in Fig. 4. There is considerable scatter of data points about the 2.6 Ga reference line, reflecting broad correlation between variations in the Re and Os isotopic compositions of different samples. Three massive chromitites have the lowest $^{187}Re/^{188}Os$ in this sample set and average $^{187}Os/^{188}Os$ of 0.11026±0.00005 (2σ) which is almost as same as the initial $^{187}Os/^{188}Os$ ratio of chondritic reference isochron.

The model age (T_{MA}) and Re depletion ages (T_{RD}) (Table 1) of each sample was calculated follows the chondritic evolution model of Os isotope composition in the primitive upper mantle (PUM). Actually, for today's value of $^{187}Os/^{188}Os$ of PUM we use two different values, one is 0.1296 (Meisel et al., 2001) very close to 0.1281 of ordinary (O) and enstatite (E) group chondrites (Walker et al., 2002a,b) for model 1, and another is 0.1270 (Shirey and Walker, 1998) very close to 0.1260 of carbonaceous (C) group chondrites (Walker et al., 2002a,b) for model 2 (Table 1). The average T_{RD} age of the samples are 2.56± 0.03 Ga (2σ) and 2.39±0.03 Ga (2σ) for model 1 and 2 respectively. Also the average T_{MA} are 2.62±0.01 Ga (2σ) and 2.45±0.02 Ga (2σ) respectively. The average model ages of three massive chromitites are 2.62 and 2.46 Ga respectively (Table 1). The Os isotope model age from ophiolitic podiform chromitite is similar to the age of the Zunhua ophiolite constrained by the tectonics of ophiolite and its relationships to wall rocks and intrusive rocks (Kusky, 2004). The formation age of Zunhua ophiolitic chromitite is consistent with regional structural relationships. U–Pb isotopic ages for other components of the Zunhua structural belt in the area include 2561 and

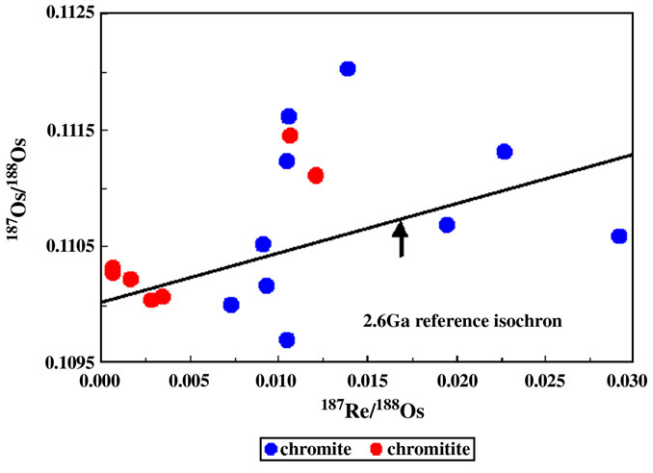

Fig. 4. Re–Os isotope data for the Zunhua ophiolitic podiform chromites and chromite separates.

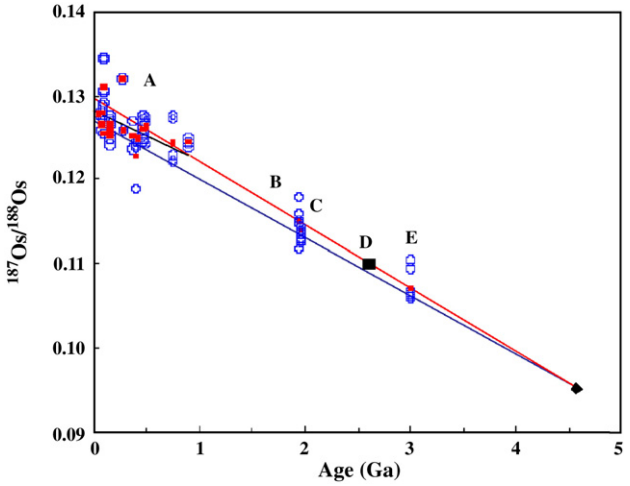

Fig. 5. Os isotopic evolution of the convecting upper mantle. A refers to the initial $^{187}Os/^{188}Os$ ratios and average of ophiolitic podiform chromites of each age separated from 18 ophiolites (Walker et al., 2002a,b). The short line is the least squares linear regression of the age of chromite formation versus initial $^{187}Os/^{188}Os$ of chromite with deferent ages (Walker et al., 2002a,b). B is the initial $^{187}Os/^{188}Os$ ratios and average for 5 podiform chromitites from two boulders in the Jormua ophiolitic complex of northern Finland (Tsuru et al., 2000). C is the initial $^{187}Os/^{188}Os$ ratios and average for podiform chromite separates from the Paleoproterozoic Outokumpu ophiolites of northern Finland (Walker et al., 1996). D shows the average of Os isotopic compositions for 3 massive chromitites from Zunhua Archean ophiolitic podiform chromitites. E is the initial $^{187}Os/^{188}Os$ ratios and average for ophiolites, chromitites and chromite separates from the Lipovenki and Kapitanov, Ukrainian Shield (Gornostayev et al., 2004), 3.0 Ga was deduced based on Os model age and not independent as other ophiolites plotted on this figure. Two lines describe the chondritic evolution trajectory of convective upper mantle. Upper line is for modern value of $^{187}Os/^{188}Os$ of 0.1296 similar to ordinary and enstatite chondrites. Lower line is for carbonaceous chondrite with modern $^{187}Os/^{188}Os$ ratio of 0.1270. Two lines converge to the Os isotopic composition of iron meteorite. This long curve describes the chondritic evolution of the convective upper mantle.

2560+6/−4 Ma for tonalitic gneisses (Wang et al., 1995), 2501+19/−17 Ma for trondhjemitic gneisses (Regional Geological Survey Team of Hebei, 1988), and 2576+29/−23 Ma for biotite gneisses. All these ages represent the lower limit for the emplacement age of ophiolites, as they are cut by the ophiolitic mélange fabric. Red granites intruded into the ophiolitic complex zone are products of the collision (Kusky and Li, 2003), and have a U–Pb (zircon) age of 2400±15 Ma (Wu et al., 1992), representing an upper limit for the formation age of the ophiolites. It is inferred from these isotopic ages and regional relations (Kusky et al., 2001; Kusky and Li, 2003; Kusky, 2004) that the Zunhua ophiolitic mélange belt was emplaced at about 2.5 Ga. So that the formation age of ophiolites is constrained between 2.5–2.7 Ga, consistent with the Os isotopic model age.

5. Discussion

Re and Os are refractory and highly siderophilic elements in cosmochemical and geochemical classifications of the elements. During early stages of solar system evolution both were preferentially segregated into solid phases as planetesimals accreted from the solar nebula. During early fractionation of the Earth they were almost completely segregated into the core. The small quantities of Re and Os present in the silicate earth are thought to be derived from late veneer processes by which late accretionary meteorites delivered Re and Os to the Earth's mantle towards the end of accretion, after core formation (Plame et al., 2003).

Traditionally the evolution of Os isotopic composition for primitive upper mantle was modeled as a chondritic type with proper initial and modern $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ ratios. There are two sets of parameters to describe the chondritic evolution of PUM. In the first set the modern $^{187}Os/^{188}Os$ is 0.12700 from carbonaceous chondrite (Luck and Allegre, 1983; Walker et al., 2002a) and $^{187}Re/^{188}Os$ is 0.40186 (Shirey and Walker, 1995). In the second set the modern $^{187}Os/^{188}Os$ is 0.1296±0.0008 from the best estimate for modern value of PUM via Cenozoic basalt-born mantle peridotites worldwide (Meisel et al., 2001) and similar to enstatite and ordinary chondrites (Meisel et al., 1996, 2001; Walker et al., 2002a,b) and $^{187}Re/^{188}Os$ is 0.435±0.005 (Peng et al., in press). But both shared the common initial $^{187}Os/^{188}Os$ ratio of 0.09531 for early solar system materials (Shirey and Walker, 1998). However the initial $^{187}Os/^{188}Os$ ratio of iron meteorites varies within a small range from 0.0946–0.09609 with an average of 0.09556±0.00042 (σ, n=14) (Cook et al., 2004). These two evolution trajectories of Os isotopic compositions in the convective upper mantle are plotted as Fig. 5. The difference of Os isotopic compositions between two models is decreasing from 2% in modern times until they converge at the age of the formation of the Earth. We calculated Os isotopic model ages T_{MA} and T_{RD} for the Zunhua ophiolitic podiform chromitites and chromite separates based on these two evolution trajectory of PUM (Table 1). All model age data only vary in a small range due to very low $^{187}Re/^{188}Os$ ratio of chromitites and their separated chromites (Table 1).

The Os isotopic composition and evolution of the convective upper mantle is interesting and a significant research subject relative to differentiation of the mantle during its partial melting and the fate of the subducted oceanic lithosphere.

Information about the Os isotopic compositions of the modern convective upper mantle can be obtained from several sources including Mid-Ocean Ridge Basalts and their related glasses and sulfides (Martin, 1991; Roy-Barman and Allegre, 1994; Snow and Reisberg, 1995; Brandon et al., 2001; Escrig et al., 2005), and abyssal peridotites. The measurements of MORBs and related glasses and sulfides have revealed a very large range of Os isotopic compositions varying from 0.1314 to 0.2316 (Walker et al., 2002a,b; Escrig et al., 2005) that is much higher than the modern value of carbonaceous, enstatite and ordinary chondrites (Shirey and Walker, 1998; Meisel et al., 1996, 2001). Such radiogenic compositions are interpreted either as the result of seawater contamination (Shirey and Walker, 1998; Walker et al., 2002a,b) or as the result of in situ decay of ^{187}Re into ^{187}Os (Shirey and Walker, 1998; Walker et al., 2002a,b). Abyssal peridotite represents the uppermost part of depleted residue left after MORB generation in the convective upper mantle. The $^{187}Os/^{188}Os$ ratios measured in abyssal peridotites range from 0.120 to 0.129 (Martin, 1991; Roy-Barman and Allegre, 1994; Snow and Reisberg, 1995; Brandon

et al., 2001) averaging 0.1247, and it is unradiogenic compared to that of modern value of MORB, chondrites and PUM (Meisel et al., 1996, 2001). The Os isotopic compositions of convective upper mantle reflects melt extraction from the primitive upper mantle and recycling of crust materials. The present convective upper mantle is highly heterogeneous (Meibom et al., 2002).

Ophiolites of different formation ages represent a very significant resource for information about the Os isotopic compositions of convective upper mantle in Earth history. Podiform chromitites and chromite separates obtained from ultramafic mantle tectonite and overlying crust sequences of the ophiolites typically yield the most important information for Re–Os studies. Chromites are often the only primary magmatic phase that survives the alteration processes and tend to incorporate Os and exclude Re during ophiolite formation. Chromites normally have both very low Re/Os ratios and elevated Os concentrations, and consequently only need limited age correction for definition of the initial Os isotopic ratio of the convective upper mantle source from where the ophiolite was derived. Also, high Os concentrations means that the Os isotopic compositions of chromites are difficult to modify through the subsequent seafloor alteration and obduction processes (Walker et al., 2002a,b).

There are several cases of reported Os isotopic compositions of convective upper mantle in Phanerozoic and Proterozoic Era via the measurement of Os isotopic ratios of podiform chromitites and chromite separates from ophiolites (Walker et al., 1996; Tsuru et al., 2000; Walker et al., 2002a,b; Gornostayev et al., 2004). Walker et al., 2002a,b reported Re–Os isotopic systematics of chromites separated from the upper mantle or low crust portions of 18 ophiolites ranging in age from 900 Ma to 50 Ma and in tectonics including both MOR and SSZ settings. The calculated initial γOs values of the entire group varied in a limited range averaging +1.31. Least squares linear regression of the age of chromite formation (in Ga) versus initial Os isotopic ratio of a filtered suit yield a slope of -0.0058 ± 0.0019 (2σ) and a present day intercept of 0.12809 ± 0.00085 (2σ), equivalent to γOs value of $+0.9\pm0.6$. Of the suite of 51 samples analyzed, 68% lie within ±1% of this evolution trajectory (Walker et al., 2002a,b). The trajectory is plotted between the two PUM evolution lines for Model 1 and 2 on Fig. 5. The present value 0.12809 of Os isotopic ratio in the chromite trajectory is between the modern values of primitive upper mantle of 0.1296 ± 0.0008 from the Cenozoic basalt-born peridotite xenoliths worldwide (Meisel et al., 2001) which is similar to that of enstatite and ordinary chondrites and of 0.1270 from the carbonaceous chondrite (Meisel et al., 1996, 2001). Most of the calculated initial Os ratios of samples, especially for the average initial ratios for each ophiolite are plotted on the area between two evolution trajectories described based on the Os isotopic compositions of iron meteorites and enstatite, ordinary and carbonaceous chondrites (Fig. 5). Broadly, the Os isotopic compositions of Phanerozoic convective upper mantle where the ophiolitic podiform chromitites were derived from are consistent to the Os isotopic composition range of chondrites.

Walker et al. (1996) reported Os isotopic data for gersdorffite, laurite and chromite separates from the upper mantle section of the 1.97 Ga Outokumpu ophiolite, eastern Finland. The initial Os isotopic compositions of 11 chromite samples vary from 0.11267 to 0.11428, and the average of 0.11328 is plotted on Fig. 5. This indicates that the mantle sources of these materials were broadly chondritic (within ±2% of projected chondrite compositions) in their long-term Re–Os isotopic evolution (Fig. 5).

Tsuru et al. (2000) reported that complex Re–Os isotopic systematics of whole rock serpentinites, disseminated oxides separated from serpentinites, and podiform chromitites from the mantle portions of the circa 1.95 Ga Jormua ophiolite complex, northeastern Finland, may be related to its complicated and polyphase tectonic setting (Peltonen et al., 2000; Kusky, 2004) and open-system isotopic systematics (Tsuru et al., 2000). The five samples from two chromitite boulders found in the Antinmaki part of the Jormua ophiolite complex show closed-system Re–Os isotopic systematics. Five calculated initial Os isotopic ratios range from 0.11165 to 0.11780 (average of 0.11504) plot on a slightly wider range than that limited by chondrite evolution trajectory on Fig. 5, but the average ratio of five samples falls in the area between the two chondrite trajectories (Fig. 5).

Gornostayev et al. (2004) reported the Re–Os isotopic data of ophiolitic podiform chromitites from the Liovenki and Kapitanov massifs in the Golovanevsk suture zone, Ukrainian Shield. The initial Os isotope ratios of 3 whole rock chromitite and 8 chromite separates range from 0.10587 to 0.11028 average 0.10708 (Fig. 5). Assuming the Archean ophiolitic mantle was chondritic, the 3.0 Ga formation age of the ophiolite was deduced (Fig. 5).

In this study, we report the Re–Os isotopic systematics of ophiolitic podiform chromitites and chromite separates from Zunhua ophiolite mélange, North China. Of 17 samples three massive chromitites have very high Os concentration in the range from 316 to 354 ppb and very low $^{187}Re/^{188}Os$ ratios from 0.0007 to 0.0017, so that their $^{187}Os/^{188}Os$ ratios are well-constrained initial ratios. The formation age of the Zunhua ophiolite is constrained to 2.5 Ga, late Archean by regional geological history and geochronology of various rocks. From Fig. 5 it is obvious that the nature of the late Archean convective upper mantle was chondritic in Os isotopic composition.

Fig. 5 shows the chondritic evolution of Os isotopic compositions for the convecting upper mantle. Ophiolitic podiform chromites and chromite separates show a chondritic Os isotopic evolution that we can now extend from the Phanerozoic (A on Fig. 5) and Proterozoic (Band C, Fig. 5) back into the Archean using the samples from the Zunhua ophiolite (D on Fig. 5). These represent the first reported chondritic Os-isotope compositions for Archean ophiolitic chromitites, and thus the convecting upper mantle, extending the known chondritic isotopic evolution of the upper mantle by more than 500 million years.

6. Conclusions

The Zunhua chromitites are typical ophiolitic podiform chromitites (Walczyk et al., 1991; Gornostayev et al., 2004).

The nodular and orbicular chromites are variably deformed, from strongly-stretched to weakly reworked, characteristic of ophiolite chromites (Nicolas, 1989; Walker et al., 2002a,b) that accumulate below the transition between oceanic crust and mantle. Inclusions within chromites and Opx of the host peridotites record high-temperature mantle deformation. Flattening and elongation of chromitite parallel to foliation and lineation also result from intense high-temperature shearing in the upper mantle.

Comparison between the Zunhua chromite ores and younger examples reveals a surprising similarity in textures, structures, and mineral compositions. Podiform chromitites are present almost exclusively in ophiolites, being generated in the uppermost oceanic mantle beneath active spreading ridges or intraoceanic suprasubduction zone (Lago et al., 1982; Leblanc and Nicolas, 1992). The documentation of the Zunhua chromitites provides convincing evidence for the operation of sea-floor spreading and plate tectonics during the Archean. $^{187}Os/^{188}Os$ ratios of podiform chromitites separated from different ophiolites record Os isotopic compositions of the convecting upper mantle. The $^{187}Os/^{188}Os$ ratios of three massive chromitites having highest Os concentrations (>300 ppb) in the Zunhua ophiolite range from 0.11021 to 0.11030, averaging 0.11026±0.00004, between 0.11034 (model 2, Fig. 5) and 0.10921(model 1, Fig. 5) at T=2.6 Ga, providing a new data point for understanding the Os isotopic composition of the convecting upper mantle in Archean. Significantly, the chondritic Os isotope composition deduced from ophiolite podiform chromitites is also the oldest reported, showing that plate tectonic processes created and recycled oceanic crust in Earth's early history.

Acknowledgements

We are grateful to Jun Feng and Xianglong Niu for the assistance during many field excursions. This work was supported by the U.S. National Science Foundation (awards no. 02-07886, and 01-25925 to T. Kusky, by Peking University (to Jianghai Li) and the National Natural Science Foundation of China (Grant No. 40173009 and 49873005), National Grant No. G1999075503, and Knowledge Innovation Program of Chinese Academy of Sciences (Grant No. KZCX2-107) to Xiachen Zhi. We also thank Zhao Wan Quan, Mayor of Zunhua County for his logistical help in the field.

Rick Carlson is thanked for his instruction and supervision of Re and Os data collection in the DTM at Carnegie Institution in Washington D.C., USA. Qing X, Zheng L, and Meng Q, from the Re–Os isotopic geochemistry laboratory in school of Earth and Sciences, USTC of China are thanked for their laboratory contributions to author Xia Q.X. Prof. Peng Z.C. is thanked for his instruction and help in Os measurement via NTIMS, Gao J.F. from the Department of Earth Sciences, Nanjing University for his assistance in Re measurement via ICP-MS. Richard Walker and John Encarnacion are thanked for thoroughly reviewing the early version of this manuscript and the many suggestions to improve the manuscript's quality.

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