Mantle metasomatism for metaperidotite from Shuanggou ophiolite of Yunnan Province by proton microprobe*

Chen You-Hong (陈友红), Zhu Jie-Qing (朱节清), Wu Xian-Kang (邬显慷), Gu Ying-Mei (谷英梅), Li Xiao-Lin (李晓林)
(*Shanghai Institute of Nuclear Research, the Chinese Academy of Sciences, Shanghai 201800*)
Zhang Qi (张　旗), Xu Ping (徐　平) and Li Xiu-Yun (李秀云)
(*Institute of Geology, the Chinese Academy of Sciences, Beijing 100029*)

Abstract This study shows that olivine, serpentine and orthopyroxene are enriched with compatible element Ni; clinopyroxene with Ni and Y; spinel strongly with Ni, Zn, Ga, Ge, As and Zr; chlorite with Ni ,Zn, Sr and Zr. However, grossularite is poor in all of these trace elements, except Sr. The trace element composition and distribution in the minerals are heterogeneous. The distributions of trace elements in the minerals further demonstrate that they result from mantle metasomatism under open system.

Keywords Ophiolite, Mantle metasomatism, Proton microprobe, Micro-PIXE, Trace element composition and distribution

1 Introduction

In recent years geologists have put forward several models to explain the mantle heterogeneity in chemistry. As one of these models, mantle fluid or melt metasomatism may result in the mantle heterogeneity [1]. Understanding mantle fluid or melt metasomatism of different areas may help to provide an important information on the mantle composition and evolution. In metaperidotite of Shuanggou ophiolite, mantle metasomatism was obviously observed under microscope [2]. Samples from this area were previously analyzed for major, trace elements and Nd, Sr, Pb, O isotopic composition by whole-rock geochemical techniques [2–4]. In this paper we used proton microprobe and quantitative micro-PIXE analysis technique with high spatial resolution and low detection limits for element mapping and quantitative analysis to determine trace element composition and distribution in micron-scale area of minerals crystallized by fluids or melt from metaperidotite of Shuanggou ophiolite. Fine-scale trace element variation reported here may provide additional important information on mantle metasomatism.

2 Geologic setting

The Shuanggou ophiolite is exposed in the middle part of Ailaoshan ophiolite belt located between the eastern Yangtze Massif and western Lincang Massif. The Shuanggou ophiolite is composed of three petrologic units: meta-peridotite (plagioclase lherzolite and spinel harzburgite) in the lower, gabbro and diabase in the middle, and basalt in the upper[5].

The phenomenon of fluids or melt metasomatism in Shuanggou metaperidotite was well observed under microscope. An obvious evidence is that a lot of white vermicular bodies (2mm to 1cm wide and 2cm to 5cm long) and melted droplets can be seen in plagioclase-lherzolite. They are composed of clinopyroxene, grossular, chlorite,spinel and minor epidote and serpentine. Of all these minerals, clinopyroxene and spinel are original minerals; chlorite is the product of devitrification of glasses; grossularite, serpentine and epidote may be formed by alteration of melt droplet[2].

3 Experimental and analytical procedures

Samples investigated in detail are from the metaperidotite at the bottom of Shuanggou ophiolite. Samples were made into doubly-

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polished thin sections and glued onto a piece of glass slide. The surface of sample was coated with a thin layer of carbon film to reduce charge accumulation and damage on the sample.

The investigation was done with the proton microprobe at Shanghai Institute of Nuclear Research[6]. The energy of proton beam for micro-PIXE analysis was chosen as 3.0 MeV to obtain a good ionization cross section and reasonable background for most elements of interest in micron scale areas of minerals. The beam current was 50~100pA, focused beam spot diameters were ca 5μm for point analysis and 15μm for scanning analysis. A Si(Li) detector was mounted at an angle of 135° with respect to the direction of the beam to collect the characteristic X-rays of elements. An optical microscope positioned over the specimen chamber and an on-line scanning graphic monitor were used to observe and monitor the region of interest measured. In order to improve detection sensitivity of trace elements, a piece of 110μm thick Al filter was used to attenuate major element lines ($Z \leq 26$) which interfered lines of some trace elements. For point analysis X-ray spectrum of each point was recorded, then peak area of element was calculated off-line using AXIL program, and thereby trace element concentration was calculated using Fe as internal standard element by TTSPM program[7]. For scanning analysis data of about one million events containing X-ray energy (E) and scanned position (x, y) information for each event were accumulated into an unsorted data file on the computer, a sorting program was used to produce concentration distribution maps for all elements present in the scanning area[8].

4 Results and discussion

4.1 Quantitative point analysis

In this study we determined the trace element composition in minerals including olivine, serpentine, orthopyroxene, clinopyroxene, spinel, grossularite and chlorite from Shuanggou metaperidotite. Except olivine and orthopyroxene (existed as mantle relic minerals), the other minerals were crystallized by fluids or melt. According to data in Table 1 olivine and serpentine are strongly enriched with Ni; orthopyroxene also with Ni; spinel with Ni, Zn, Ga, Ge and Zr; chlorite with Ni, Zn, Sr and Zr; clinopyroxene only with Y; whereas grossularite is almost poor in all of the trace elements excpet with Zn and Sr. Accordingly, it demonstrates that spinel and chlorite are the major mineral phases concentrating trace elements.

Olivine in Shuanggou metaperidotite is mantle-derived relic mineral[2]. Ni-enrichment in olivine is consistent with previous view.The similarity of trace element contents in serpentine to those in olivine suggests that there are no obviously variation of trace element distribution in the process of serpentinization. The anomaly concentration of Ni in chlorite may be considered to have two kinds of different explanation: (a) initial mantle fluids (or melt)were enriched with Ni, and they were derived from deep level of mantle; (b) mantle fluids mixed with surrounding materials while its raising, and thereby made Ni abundance in fluids very high. As we have known, fluid enriched with Al could produce reaction with olivine, and then formed chlorite, which can be expressed as:Olivine+Al_2O_3+$H_2O$$\rightarrow$ Chlorite. Therefore, the anomaly concentration of Ni in chlorite may be explained. Additionally, chlorite in Shuanggou mantle peridotite strongly concentrates on Mg, this may be associated with the origination of chlorite from deep level of mantle. Based on these evidences, the above second explanation might be more reasonable. Combined with isotope (Nd, Sr, Pb, O) data of Shuanggou ophiolite and mantle fluids [3,4], we further deduce that mantle fluids in Shuanggou mantle peridotite could be derived from the interface between upper mantle and the lower.

Trace elements enriched in spinel include compatible element Ni, incompatible Zr, and chalcophile Zn, Ga, Ge and As. The phenomenon of these different indicating trace elements enrichment in spinel was little reported before. The high content of Sr in grossularite (86 to 145μg/g) was probably associated with alteration of Ca-rich plagioclase. Grossularite in Shuanggou mantle peridotite was formed by alteration plagioclase[2]. According to data reported before partition coefficient of Sr in plagioclase is 1.8[9], thus plagioclase is enriched with Sr and thereby high-Sr resulted in grossularite.

4.2 Trace element distribution in micron-scale area of minerals

In order to obtain trace element distribution in micron-scale area of minerals, we selected clinopyroxene and chlorite of sample No. MS4-5 for scanning analysis. Fig.1 shows the ×100 photomicrograph of sample No.MS4-5. A region of interest with an area of 60μm x410μm was chosen for micro-PIXE analysis. As seen in Fig.2(a), the distributions of Ni and Sr are different from that of Zn in chlorite, and no correlation can be seen for each other. The different distributions of Ni and Zn suggest that trace elements in chlorite are controlled by different

Table 1 Representative major elements and trace elements analysis of minerals

MS-	Olivine		Serpentine		Orthopyroxene		Clinopyroxene		Spinel		Grossularite		Chlorite	
series	4-3	4-3-1	4-5	4-5-1	20-2	4-6	20-1	4-5	20-1	4-3	20-1	20-2	20-1	4-5
SiO_2	41.545	40.518	46.34	39.795	55.435	54.063	52.725	52.182	0.069	0.038	37.392	38.317	33.835	37.961
TiO_2	0	0	0.071	0.072	0.353	0.177	0.504	0.360	0.440	0.509	0.156	0.350	0.302	0.
Al_2O_3	0.033	0	2.256	2.933	2.172	3.976	4.278	3.096	23.696	26.527	21.814	22.689	11.294	8.049
Cr_2O_3	0	0	0.496	0.027	0.298	0.720	0.351	1.003	35.771	34.195	0.145	0	0.285	0.199
FeO	9.568	9.751	6.463	2.577	6.747	5.972	2.864	2.582	27.747	23.269	0.696	0.432	5.576	4.610
MnO	0.053	0.128	0.085	0.023	0.278	0.171	0.129	0.129	0.433	0.238	0.101	0.102	0.302	0.171
MgO	47.854	48.821	32.63	36.546	32.388	33.061	18.169	18.174	10.656	13.783	0.082	0.096	35.133	34.120
CaO	0.052	0.045	1.361	0.053	1.921	1.201	21.243	22.069	0.018	0.006	37.290	36.918	0.117	0.079
Na_2O	0.033	0.047	0.030	0.021	0.022	0.015	0.319	0.450	0.042	0.040	0	0.029	0.048	0.007
K_2O	0.010	0.002	0.018	0.009	0.018	0	0	0.004	0	0.015	0	0	0.002	0.005
Total	99.148	99.312	89.69	82.056	99.632	99.356	100.582	99.989	98.872	98.620	97.676	98.933	86.894	85.201
Ni	2844	2869	2263	2318	575	639	233	296	1029	1048	–	–	1503	1683
	(18)	(24)	(16)	(20)	(21)	(19)	(9)	(7)	(43)	(24)	–	–	(22)	(61)
Cu	–	–	6(3)	18(3)	–	–	–	–	–	–	–	–	–	–
Zn	27	21	29	34	45	39	13	8	1768	1088	25	43	134	106
	(2)	(2.4)	(2)	(2.6)	(5)	(3.8)	(1.3)	(1.5)	(15)	(13)	(1)	(1.2)	(3)	(5)
Ga	–	–	–	–	–	–	7(1.2)	5(1.3)	116(8)	49(4.6)	8(1)	13(1.3)	–	–
Ge	–	–	–	–	–	–	8(1.3)	–	70(8)	–	–	–	–	–
As	–	–	–	–	–	–	–	–	54(9)	5(3.6)	–	–	–	–
Sr	–	–	–	11(1.7)	–	–	–	6(2.1)	21(8)	–	86(1.4)	145(2.3)	38(19)	10(4)
Y	–	–	–	–	–	–	–	28(2.8)	–	–	–	–	–	–
Zr	–	–	–	–	–	–	–	–	51(25)	–	4(1.4)	6(2.1)	34(15)	–

Notes: Oxides in mass percentage determined by electron microprobe; trace elements in μg/g, by micro-PIXE analysis. Bars denote below detection limits. Figures in parentheses are standard deviations(1 σ) for analyses.

factors, respectively. For clinopyroxene the distribution of Ni presents local enrichment, suggests that Ni-rich inclusions (e.g. olivine) may be trapped in that micron-scale area. Comparing Fig.2 (b) with Fig.2(a), we further found that the distributions of Cr, Ni and Zn were consistent with their relative distribution, displaying local enrichment or zoning. This suggests that the distributions of trace elements in micron-scale area are heterogeneous, and the heterogeneity may result largely from metasomatic process of mantle fluids.

5 Conclusion

The study shows that proton microprobe provides an ideal means to determine trace element composition and distribution with micron scale areas of minerals. The experimental results show that: (a) The relic minerals such as

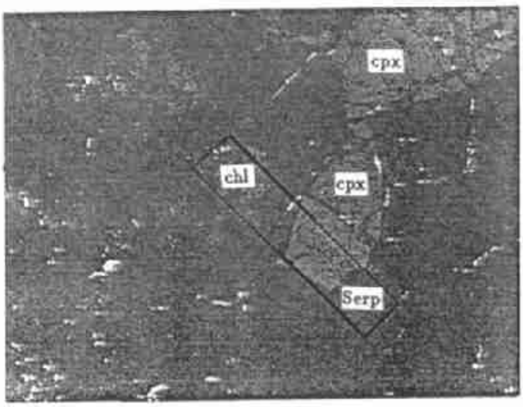

Fig.1 Photomicrograph of scanning area in minerals of sample No.MS4-5

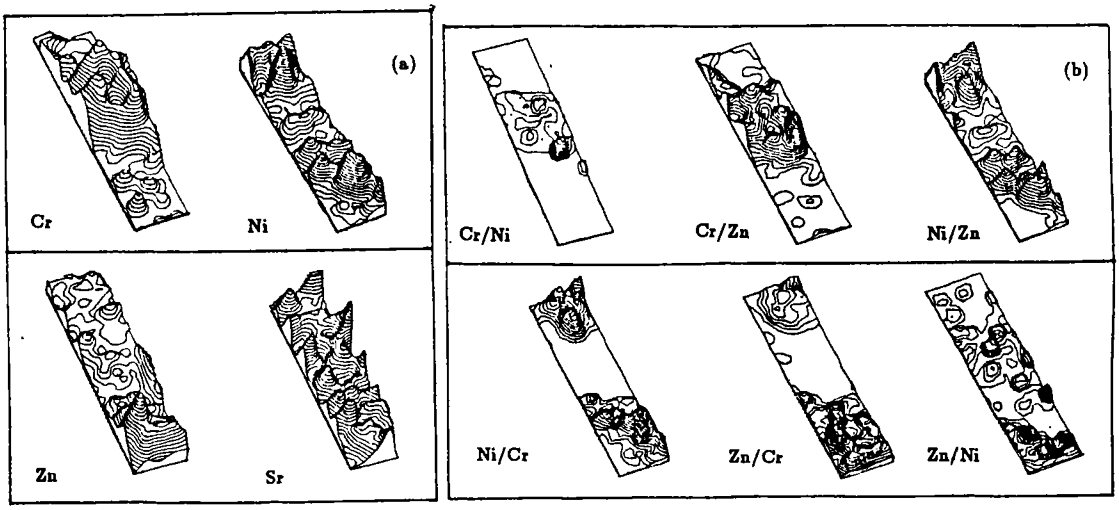

Fig.2 Partial elemental maps in micron areas of clinopyroxene and chlorite of sample No. MS4-5(a) and mole ratio distibution maps of trace elements in scanning areas(b)

olivine and orthopyroxene from Shuanggou mantle peridotite are mainly enriched with compatible element Ni; grossularite only with Sr, which could be related to crystal chemical feature of grossularite; the trace element characteristics of serpentine is similar to olivine, indicating in the process of serpentinization large-ion-lithophile elements (LILE) were obviously not added into minerals; (b) Both spinel and chlorite crystallized by mantle fluid were strongly enriched with Ni; the high-Ni contents in chlorite result from metasomatism of mantle fluid; besides, spinel was also enriched with chalcophile elements (Zn, Ga, Ge, As), suggesting the existence of inclusions of sulphide which is micron order of magnitute in size; (c) The heterogeneity of trace element distribution in micron-scale area of minerals can be considered to have two aspects of explanation: one is associated with the existence of micrograined inclusions (such as olivine); the other is due to the infiltration process of solution in mantle metasomatism. O'Reilly et al[10] demonstrated that trace element distribution in rock was decided by whether diagnostic minerals concentrating those trace elements, existed or not. They also inferred that the heterogeneity of element distribution was resulted from mantle metasomatism where spinel lherzolite was in open system, which caused silicate melt to be diluted in the process of infiltration, and caused different minerals to produce metasomatic zoning[10]. It is worthwhile to illustrate that the problem with regard to heterogeneity of trace element distribution remains to be further studied by us.

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