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# Application of nuclear microprobe to the study of metasomatism in mantle peridotites

Youhong Chen <sup>a</sup>, Jieqing Zhu <sup>a,\*</sup>, Rongrong Lu <sup>a</sup>, Xiankang Wu <sup>a</sup>, Yingmei Gu <sup>a</sup>,  
Xiaolin Li <sup>a</sup>, Qi Zhang <sup>b</sup>

<sup>a</sup> Shanghai Institute of Nuclear Research, CAS, P.O. Box 800-204, Shanghai 201800, China

<sup>b</sup> Institute of Geology, CAS, Beijing 100029, China

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## Abstract

In recent years, some models have been proposed to explain the chemical heterogeneity of the earth mantle. Among them the metasomatism by the mantle fluid and the mantle melt is the most popular one. The trace elemental behavior of the mantle minerals from different areas in micron scales can provide important information on the understanding of the mantle metasomatism. This paper describes the study of the metasomatism in mantle peridotites from Raobazhai, Anhui Province of China by the nuclear microprobe. The concentrations and distributions of trace elements in the metasomatized mantle peridotite were determined quantitatively by the micro-PIXE software package TTSPM. The internal standard and the integrated iterative method were used for the calculation. The matrix elements in the minerals were analyzed by EPMA. The accuracy of the quantitative analysis was examined by three geochemical standards of rocks (GSR). The results were better than 15% for most elements. According to the elemental maps, the trace element distributions in the amphibole, which was crystallized from the mantle fluid, displayed obvious heterogeneity and zoning. The enrichment of Ni, Zn, Ga, Rb, Sr, Y, Zr and Pb in the mineral could be associated with the metasomatism of the mantle fluid. The local coexistence of Ni, Cu, Pb, Fe and S in the amphibole suggested that there were xenoliths trapped in the minerals during their crystallization. The characteristics of the trace element composition and distribution in the mantle peridotites demonstrated that the metasomatism by the mantle fluid and the mantle melt might change the chemical composition of the mantle peridotites and thus resulted in the chemical heterogeneity of the earth mantle. © 1997 Elsevier Science B.V.

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## 1. Introduction

Some models have been proposed to explain the chemical heterogeneity of the earth mantle [1]. Among them the metasomatism by the mantle fluid or the mantle melt is the most popular one [2]. It is a great challenge for geologists to deduce the structure

and chemistry of the earth's interior from the investigations of the geochemical and petrography signatures recorded in the rocks near its surface. The conventional methods used for the study of the mantle metasomatism mainly involve observation by optical microscope, whole-rock chemical analysis and microscopic analysis by EPMA. However, none of them can provide trace element composition and distribution on micron scale areas of the minerals. The major and minor elements which are the principal constituents of the minerals are often crystal-

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\* Tel.: +86 215 9553 998/271; fax: +86 215 9553 021;  
e-mail: jqzhu@fudan.ac.cn

chemically controlled. It constrains their variability in the metasomatism process and makes the process more complicated. Because of that, the major and minor elements have been limited for use as indicators of the chemical or physical evolution of the mantle peridotites. Trace elements are less constrained by the mineral phases. Their behavior on a micron scale in the mantle minerals can provide important information on the understanding of the mantle metasomatism and its evolution.

The nuclear microprobe is well suited to determine the trace element composition and distribution in minerals of mantle rock samples because of its high sensitivity for multi-elemental analysis and high lateral resolution. It can therefore provide more detail information on the trace element behaviors indicating the metasomatic process of the earth mantle.

The nuclear microprobe had been previously used to study the mantle mineral phase transformation during metasomatism with samples of Suoluoshu mantle peridotite from the Shandong province of China [3]. The study showed that the trace element composition and distribution had obvious changes in minerals while the mineral phase was transformed from spinel to garnet. Most of the trace elements resided in the clinopyroxene and spinel. The garnet had relatively low concentrations of trace elements. The mantle metasomatism under an open system of Shuanggou ophiolite from the Yunnan province of China was also studied by the nuclear microprobe [4]. It showed that the relic minerals were mainly enriched with the compatible elements Ni and the grossularite was only enriched with Sr, which could be related to its crystal chemical features.

This paper describes the study of the metasomatism of the mantle peridotites from Raobazhai in the Anhui province of China by the nuclear microprobe. The Raobazhai mantle rock body has previously been petrologically studied by optical microscope observation [5]. It has been found that the Raobazhai mantle rock has two remarkable features. One is the mylonitization which is widespread around the edges of the rock. The other is the metasomatic mantle cordierite which forms the rock body. There are two major minerals in the cordierite: orthopyroxene and amphibole. The orthopyroxene is the remainder of the mantle after metasomatism. In the process of the metasomatism, some minerals being

rich in  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and incompatible elements get into the mantle peridotites with the mantle fluid or the mantle melt and change their compositions. The existence of the amphibole which contains water in the mineral is a characteristic feature of mantle metasomatism. It was formed by metasomatism and recrystallization in the continental lithosphere mantle wedge at the subduction zone. In the present paper, we determine the concentrations and the distributions of trace elements in small areas of metasomatized mantle peridotite, mineral orthopyroxene and mineral amphibole by means of micro-PIXE quantitative analysis with the software package TTSPM [6]. The purpose of the work was to study the metasomatism and origin of the Raobazhai mantle rock body.

## 2. Experimental and analytical procedures

The samples investigated in detail were made into doubly-polished thin sections and glued onto a glass slide. The surface of the sample was coated with a thin layer of carbon film in order to reduce the charge accumulation and heat damage of the samples.

The experiments were performed with the nuclear microprobe at the Shanghai Institute of Nuclear Research. The energy of the proton beam for Micro-PIXE analysis was chosen as 3.0 MeV to obtain good ionization cross-sections and a reasonable background for the most interesting elements of the mantle minerals. The beam current was 100–200 pA and the focused beam spot diameters were 15  $\mu\text{m}$  for point analysis and 2.5  $\mu\text{m}$  for mapping. A Si(Li) detector located at  $135^\circ$  was used to collect the characteristic X-rays of the elements. The interesting regions in the specimen were observed and monitored by means of an optical microscope positioned at the top of the specimen chamber. An on-line scanning graphic monitor based on the X-ray collection was used to locate the focused beam exactly at relevant positions.

The major elements were determined with no absorption filters in front of the detector. However, the trace elements were determined with a 150  $\mu\text{m}$  thick Al absorption filter in order to suppress the high X-ray intensity from the matrix of the specimen and to improve the trace element detection limits. A

100  $\mu\text{m}$  thick Polycarbonate foil was put in front of the Al filter in order to avoid the possibility of nuclear reactions caused by the recoil protons hitting the Al filter. Movement of the absorption filters was controlled from the outside of the specimen chamber.

For point analysis, the micro-PIXE spectrum of an interesting point was recorded, and then the X-ray intensities of individual trace elements were calculated by means of the AXIL program. The concentrations of the matrix elements in the specimen as given by EPMA analysis were used. The element Fe was used as an internal standard element for the calculation of the trace element concentrations. The concentration calculation was based on the strategy of the integrated iterative method and the oxide calculation method. All these calculations were incorporated into the software package TTSPM for thick target SPM quantitative analysis [6]. The accuracy of the TTSPM quantitative analysis was examined by the measurements of three geochemical standards of rocks (GSR) and the results are listed in Table 1. It showed that the accuracy of the method was better than 15% for most of the trace elements.

For scanning analysis, all information concerning the X-ray energy and the coordinates of each points should be recorded as events. The off-line sorting program could pick up X-ray spectra accumulated from different parts of the scanned region of the specimen and different elemental concentration distribution maps by the energy window setting [7]. In order to get rid of any specious information in the

element maps, the contribution of the X-ray background and the interfering X-ray peaks was subtracted from the total counts within the energy window for each pixel of the element maps. The usage of the net X-ray counts has been proven to be a simple and a successful method for the true element mapping technique for the mineral specimen [8].

### 3. Results and discussion

#### 3.1. Quantitative point analysis

Table 2 shows the concentrations of trace elements in mantle cortlandite from the Raobazhai rock body determined by the nuclear microprobe. It shows that the mineral orthopyroxene is depleted in all of the trace elements except the compatible elements Ni and Zn. This is related to the orthopyroxene belonging to the refractory mineral. However, the trace elements such as Ni, Zn, Ga, Rb, Sr, Y, Zr and Pb are enriched in the mineral amphibole. Especially the concentrations of Rb, Sr, Y, Zr and Pb are almost ten times higher than the primitive mantle abundance. The enrichment of Ni may be that the amphibole partially inherits the chemical composition of its source rock. However, the enrichment of Zn, Ga, Rb, Sr, Y, Zr and Pb in amphibole is closely related to the mantle metasomatism. It is deduced that these elements enter the amphibole with the mantle fluids while the amphibole is recrystallized. Because the

Table 1  
Micro-PIXE analysis of three geological standards of rocks (ppm)

Elements	Standards					
	GSR1		GSR2		GSR5	
	PIXE	Given	PIXE	Given	PIXE	Given
Ti	1504	1720	3241	3090	3805	3950
Mn	499	463	620	604	185	173
Cu	4	3.2	62	55	38	42
Zn	30	28	70	71	52	55
Ga	20	19	19	18	21	26
Rb	426	466	40	38	230	205
Sr	118	106	887	790	103	90
Y	86	106	19	9	—	26
Zr	180	167	110	99	105	96

Table 2  
Quantitative micro-PIXE analysis of trace elements in mantle cortlandite

Minerals	Orthopyroxene		Amphibole					Pentlandite point A on Ni map	
	No. 926-2-3		No. 926-2-3		No. 926-2-5			No. 926-2-5	
	No. 926-2-3 (%)		No. 926-2-3 (%)		No. 926-2-5 (%)			No. 926-2-5 (%)	
H <sub>2</sub> O	–	–	2.06	2.06	2.09	2.07	–	O	1.09
Na <sub>2</sub> O	–	–	1.75	0.90	1.72	1.66	0.97	Si	0.595
MgO	33.4	33.9	17.8	17.5	18.4	17.9	17.5	Cr	0.888
Al <sub>2</sub> O <sub>3</sub>	2.87	1.71	12.2	12.8	11.7	11.9	12.9	S	37.9
SiO <sub>2</sub>	55.4	56.5	44.9	44.8	45.9	45.1	45.1	Fe	28.4
K <sub>2</sub> O	0.06	–	0.36	0.39	0.39	0.36	0.46	Ni	31.1
Cl	–	–	0.25	–	–	–	–		
CaO	0.43	0.302	12.5	12.8	12.8	12.5	12.5		
TiO <sub>2</sub>	0.11	0.033	0.647	0.93	0.651	0.646	0.75		
Cr <sub>2</sub> O <sub>3</sub>	0.05	0.0419	0.373	0.58	0.512	0.521	0.66		
MnO	0.20	0.131	–	–	0.0787	–	–		
Fe <sub>2</sub> O <sub>3</sub>	–	0.996	–	–	–	–	–		
FeO	7.38	6.51	4.39	4.41	4.43	4.70	4.05		
	(ppm)		(ppm)		(ppm)			(ppm)	
Ni	365	277	590	586	590	774	553		
Zn	29	22	13	7	7	–	–	Zn	2327
Ga	–	–	8	7	8	7	6		
Rb	–	–	13	14	14	12	10	Cu	3113
Sr	–	–	228	232	234	235	204		
Y	–	–	90	18	18	7	6	Pb	1638
Zr	–	–	114	22	23	–	–		
Pb	–	–	114	138	140	132	137		

Void bar means that the concentration is lower than the MDL. Oxides in weight % are determined by EMPA and chemical analysis.

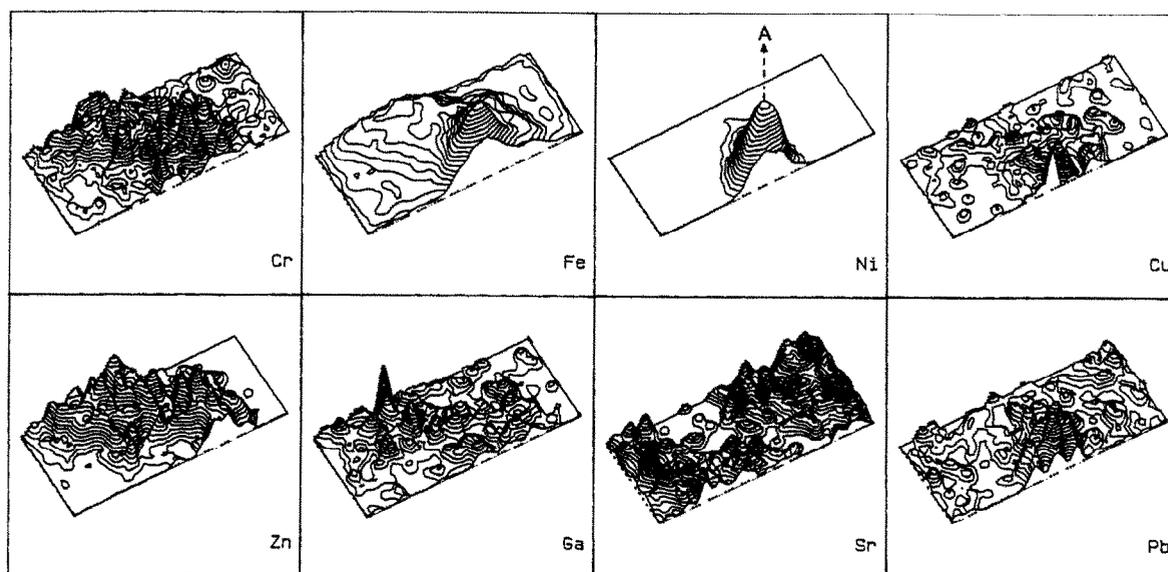


Fig. 1. Elemental concentration distribution maps in the mantle mineral of an amphibole (200  $\mu\text{m}$  by 500  $\mu\text{m}$ ).

trace elements Rb, Sr, Pb are Large Ion Lithophile Elements (LILE), Y belongs to the element of Heavy Rare Earth Element group (HREE), Zr is a High Field Strength Element (HFSE), and they are all incompatible elements, they can all enter the metasomatized fluids easily. Because of that, the enrichment of these elements in amphibole can be explained. The concentrations of Rb and Pb are high in the continental crust, therefore the enrichment of Rb and Pb in the amphibole means that the materials from the continental crust may be added into the metasomatized minerals.

According to the results, it can be deduced that the formation of amphibole and the origin of the Raobazhai rock body are both associated with the metasomatism by the mantle fluids and the continental lithosphere mantle wedge on the subduction zone which is consistent with the recognition by the studies of petrology and mineralogy. The existence of the mantle metasomatism is reconfirmed by the trace element composition in minerals of the mantle peridotite determined by the nuclear microprobe.

### 3.2. Elemental mapping

In order to obtain the trace element distributions in micron scale areas of the metasomatized amphibole, the scanning analysis was performed. Fig. 1 gives some elemental concentration distribution maps in an amphibole sample. From the maps we can see that the elemental concentration distributions in the amphibole present remarkable heterogeneity and metasomatic zoning. The elements Fe, Ni, Cu and Pb are well correlated with each other and present local enrichment. The distribution of Cr and Zn is somewhat similar to that of Ga. The distribution of Sr is negatively correlated with the other elements. This phenomenon indicates that the concentration distributions of the above three group elements are controlled by different factors for the mantle metasomatism. In order to study the responsibility for the correlation between the elements Fe, Ni, Cu and Pb, and their local enrichment in the amphibole, point analysis was performed with this sample. The X-ray spectrum from point A of the Ni map is shown in Fig. 2. The spectrum which was obtained without any absorption filters in front of the detector is shown in Fig. 2a. The strong X-ray peaks of the

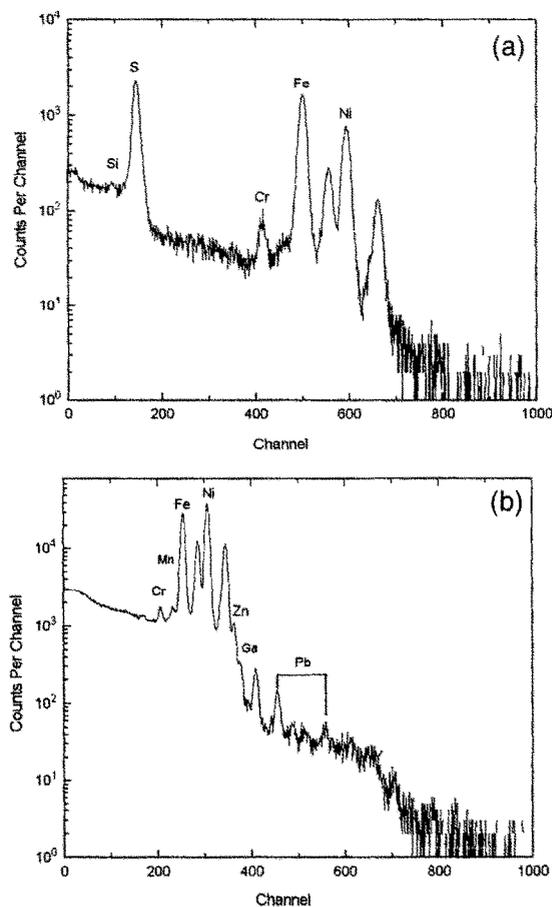


Fig. 2. The PIXE spectra obtained from the mantle mineral of an amphibole at point A on the Ni map. (a) Without any absorption filters in front of the detector. (b) With a 150  $\mu\text{m}$  thick Al foil and a 100  $\mu\text{m}$  thick polycarbonate foil in front of the detector

elements S, Fe, Ni, and Cr can be seen in Fig. 2a. They are the major components of the sample at point A. Fig. 2b shows the spectrum obtained with a 150  $\mu\text{m}$  thick Al absorption filter and a 100  $\mu\text{m}$  thick polycarbonate foil in front of the detector. The X-ray peaks of the elements Ni, Zn, Ga and Pb can be seen in Fig. 2b. The lines of Cu are not clear because of the interference by the Ni  $K\beta$  line. The concentrations of all these elements determined by the nuclear microprobe are also shown in the last column of Table 2. The results indicate that the local enrichment of Fe, Ni, Cu and Pb is caused by the existence of inclusions of pentlandite and other sulfides in the amphibole. The difference of the concen-

tration distributions among the LILE Sr, the sulphophile elements Ni, Cu, Zn, Pb and the transition elements Cr, Fe suggests that the above elements are controlled by respective geochemical affinities and the mantle fluids which induce the metasomatism have several different kinds of components. Combined, the trace element composition in amphibole determined by the quantitative point analysis with the element concentration distribution maps, it is found that the mantle fluids at least include the components of LILE Sr, sulfides (e.g. pentlandite) and elements representing the source of the continental crusts (e.g. Rb and Sr). During the metasomatic process, the elements Rb, Sr, Y, Zr could enter the amphibole with the fluids, yet the pentlandite and other sulfides could enter the amphibole in the form of micro-grain inclusions. All these characteristics of the trace element composition and distribution in the orthopyroxene and the amphibole further demonstrates the existence of the mantle metasomatism by the fluids in the Raobazhai rock body.

#### 4. Conclusions

The application of nuclear microprobe to the study of metasomatism in mantle peridotites has been successful in providing detailed information on the trace element behavior. The results indicate that the amphibole is the major mineral phase which concentrates the incompatible elements such as Rb, Sr, Y, Zr and Pb. The trace elemental distributions present remarkable heterogeneities and metasomatic zonings, which suggest the existence of mantle metasomatism by the fluids. The local enrichment of Fe, Ni, Cu and

Pb in the amphibole is caused by the micro-grain inclusions of the pentlandite and other sulfides. They enter the amphibole with the fluids during the mantle metasomatism. It can be concluded that the metasomatism by the fluids can change the chemical composition of the mantle peridotites. It results in the chemical heterogeneity of the earth mantle. This study further demonstrates that the formation of the amphibole and the origin of the Raobazhai rock body are associated with the metasomatism and the continental lithosphere mantle wedge on the subduction zone.

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