Redox state of the upper mantle

ARNOLD A KADIK

Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences,
Moscow 117975, USSR

Abstract. The oxygen fugacity condition of equilibration has been carefully determined from a spinel lherzolite from Mongolia, olivine xenocrysts from chrome pyrope-bearing peridotite nodules from kimberlites of Yakutia, and basaltic samples from ocean floor, iron arcs and the continental areas. These indicate that the spinel lherzolites occurring within alkali basalts from Mongolia, equilibrated under an f_{O_2} condition similar to that of WM buffer. The diamond and chrome pyrope-bearing peridotites from the kimberlite pipes equilibrated between IW and WM buffers. Some of the ilmenite-bearing peridotite crystallized under f_{O_2} conditions similar to that between WM and QFM buffers and chondrites equilibrated below the QFI buffer.

It is concluded that during geochemical processes in the upper mantle the f_{O_2} conditions vary broadly, and are similar to that between FMQ and IW buffers.

There is a dramatic change in the composition of the kimberlitic fluid, which is CH_4 -bearing at an early stage, but is in equilibrium with H_2O and CO_2 at a later stage. This is related to mass transfer of fluids from the lower part of the mantle with a low oxidation state to the upper part having a higher f_{O_2} condition.

Keywords. Redox state; upper mantle; oxygen fugacity; spinel lherzolite; olivine xenocryst; peridotites.

1. Introduction

The redox state of the fluid regimes of the earth's lithosphere and asthenosphere is of great importance to petrologists (Haggerty and Topkins 1985; Green *et al* 1986, Haggerty 1986, Kadik 1988). The redox state of the material at depth controls the composition of the volatile components, which in turn play a major role in the ultimate differentiation and fractionation of the melt. The generation of specific types of basaltic magmas in the mantle below a certain specific region of the ocean, formation of alkali basaltoid liquids in the rift zones and kimberlitic magmas below the cratons, lead us to the conclusion that there are specific physico-chemical regimes within the mantle, which are responsible for the production of specific types of melts. The issue now, is to evaluate the redox states of such different fluid regimes of the earth.

The discussion is focussed on the following problems: (i) Whether the lithosphere and asthenosphere are homogeneous with respect to their redox states. (ii) What were the values of oxygen fugacities during the evolution of the mantle? Whether the f_{O_2} condition was so low as to form iron and nickel-bearing phases in the early stages of mantle formation? (iii) Does the redox state of the mantle below the ocean, differ from that of the mantle below the continents? (iv) What are the factors responsible for changes in the redox regime of the lithosphere and the asthenosphere?

2. Results and discussion

One of the aspects under discussion is the nature of the fluids in the lower mantle which are introduced into the continental lithosphere and asthenosphere in the areas of formation of kimberlitic liquids. There are two contrasting views: (i) Such fluids were low in their oxygen fugacity and rich in CH_4 and became progressively oxidized during their ascent to the upper mantle (Sobolev 1977; Haggerty and Topkins 1985; Green *et al* 1986). (ii) The fluids were under higher oxidation state but underwent reduction as they came in contact with the upper mantle material (Arculus *et al* 1984).

The resolution of this problem is of crucial importance, for in the first case, oxidation of reduced fluids should result in melting.

There are several ways of determining oxygen fugacity related to mineral reactions at depth, which employ thermodynamic and experimental techniques (table 1). None of them is free from drawbacks (Ulmer *et al* 1976; Arculus *et al* 1984; O'Neil and Wall 1987; Kadik *et al* 1988; Mattioli *et al* 1990). The present study assesses the role of oxygen during reactions at depths by directly measuring f_{O_2} with electrochemical cells (for such studies refer Kadik *et al* 1988; Kadik *et al* 1989; Kadik and Zharkova 1990).

The spinel lherzolite nodules from alkali basalts of Mongolia are rather close in composition to the primitive upper mantle. The crystals are of pure gem quality and free from fluid or other inclusions (Press *et al* 1986).

The investigation also includes a study of olivines from diamond and chrome pyrope-bearing peridotite nodules within kimberlites from Yakutia. These nodules are supposed to be largely disintegrated representatives of the ancient lithosphere and asthenosphere (Pokhilenko and Sobolev 1986). Also studies on some basaltic flows from the ocean floor, island arcs and continents (Kadik and Zharkova 1990) are included.

The data obtained in the experimental runs are given in figures 1, 2 and 3. From the figures, the f_{O_2} condition of formation of the spinel lherzolites is estimated to be close to the equilibrium condition maintained by the wustite-magnetite buffer, although some of the samples reveal a slightly lower level of oxygen fugacity, close to the condition of the equilibrium of iron and wustite.

This experimental data do not agree with the rather low values of oxygen fugacity of Arculus *et al* (1984) who inferred that the samples of spinel lherzolites equilibrated under an f_{O_2} condition, which is below the IW buffer. Our observation thus contradicts their conclusion on the existence of two groups of rocks in the upper mantle; those formed under reduced condition and the other equilibrated under higher f_{O_2} conditions.

Table 1. Various methods related to the determination of f_{O_2} for reactions at depth.

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1. Thermodynamic calculations of f_{O_2} for different mineral assemblages (olivine-orthopyroxene-spinel, olivine-orthopyroxene-ilmenite, garnet-orthopyroxene-olivine and ilmenite-spinel). 2. $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in volcanic glasses as a function of f_{O_2}. 3. Presence of free graphite in fluid inclusions reflecting a particular f_{O_2} value. 4. Use of electrochemical cells to measure f_{O_2} condition of equilibration for mineralogical reactions at depth.
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Figure 1. Examples of intrinsic oxygen fugacity measurements of spinel lherzolite nodules (alkali basalts, Mongolia) and diamond and pyrope-bearing peridotite (kimberlite, Yakutia) 1: orthopyroxene, 2: olivine from spinel lherzolite, 3: olivine from sheared diamond-bearing peridotite, 4: olivine from diamond-bearing chrome peridotite. Quartz-fayalite-magnetite (QFM) buffer, wüstite-magnetite (WM) buffer, wüstite-iron (WI) buffer, quartz-fayalite-iron (QFI) buffer plotted at 1 bar.

Figure 2. Examples of intrinsic fugacity measurements of minerals and glasses from basalts and kimberlites. 1, 2, 3: olivine from alkali basalts of rift zone (Baikal lake, Iceland Africa); 4, 5: olivine from kimberlites (Yakutia); 6: glasses of alkali basalts (Mongolia).

Figure 3a. Examples of intrinsic oxygen fugacity measurements of minerals and glasses from basalts of island arcs and ocean basin: 1: Central Atlantic, 2: Indian Ocean, 3: Northern Atlantic, 4: Hawaii.

Figure 3b. Bulk rock samples of basalts from Kamchatka.

The same spinel lherzolites which were used by Mattioli *et al* (1990, also see table 2) were studied and the observations agree well with their findings. The values of oxygen fugacity as estimated for spinel lherzolites, strengthen the possibility of the existence of a graphite phase in the P-T regime, where these ultramafic rocks originally occurred. These are also the regions where basaltic magmas are generated in the mantle. This inference is of considerable importance on the composition of the fluid phase, which varies as a function pressure and f_{O_2} (figure 4).

This conclusion is confirmed by the presence of rare and extremely fine-grained crystals of graphite in minerals in the spinel lherzolite nodules included within alkali-basaltoid rocks from Mongolia. The presence of graphite was confirmed by the Raman spectroscopic techniques.

However, the possible dissolution of carbon in crystals and melts would inhibit its

Table 2. Comparison of experimental data of intrinsic oxygen fugacity for minerals of a spinel lherzolite included within alkaline basalt as xenoliths of Shavaryn-Tsaram volcano (Northern Mongolia) (Kadik *et al* 1988) with thermodynamic data carried out by Mattioli *et al* (1990) for the same samples.

Sample	Mineral	$t(^{\circ}\text{C})$	$-\log f_{\text{O}_2}$ (determined)	$-\log f_{\text{O}_2}$ (calculated)
MOZ	Ol	1011	13.22	13.20
	Opx		13.04	
	Cpx		13.42	
	Spl		13.16	
MHP 79/1	Ol	1004	13.92	13.11
	Opx		13.73	
	Cpx		13.52	
MHP 79/4	Ol	956	14.54	15.71
	Opx		14.20

Figure 4. Effects of f_{O_2} on the composition of fluid phase in equilibrium with graphite in the C-O-H system at 1200°C and pressure at 10 and 30 kb.

appearance in rocks as a separate phase. The experiments related to the interaction of graphite in olivine crystals and basaltic melts under 15 to 50 kb at temperatures between 1400 and 1800°C attest to the fact that the amount of carbon dissolved in a silicate melt and crystals may vary up to 0.01–0.10 w% (Shilobreeva *et al* 1989, Shilobreeva and Kadik 1990).

The olivines of mantle origin are saturated with respect to its graphite content (table 3), and it appears that the olivine-bearing mantle rocks were in equilibrium with graphite. The diamond and chrome pyrope-bearing peridotites from the kimberlite pipe of Udachnaya (Yakutia) reveal widely varying f_{O_2} conditions (between IW and WM buffers).

As there is progressive disintegration of the diamond-bearing peridotite xenoliths, it is considered that with the ascent of the kimberlitic fluid, the f_{O_2} condition of

Table 3. The carbon content in natural olivines determined by the $^{12}\text{C} (d, n)^{13}\text{N}$ method (1) and the method involving $^{12}\text{C} (d, n)^{13}\text{N}$ nuclear reaction plus surface contamination by means of $^{12}\text{C} (d, p)^{13}\text{C}$ reaction (2). (Shilobreeva *et al* 1987)

Rock Type	%Fo	Carbon content,	
		Wt%	Method
Nodule from spinel lherzolite (Baikal rift)	89.6	0.08 + 0.01	1
Megacryst from alkali basalt (Baikal rift)	91.4	0.04 + 0.02	1
Megacryst from picrite of pillow lava (Iceland)	89.4	0.03 + 0.02	1
Megacryst from tuff (Oldoinyo Lengai volcano, Africa)	80.5	0.04 + 0.03	1
Nodule from alkali basalt (Baikal rift)	90.5	0.038 + 0.007	2
Megacryst from alkali basalt (Shavaryn-Tsaram volcano, Mongolia)	89.9	0.09 + 0.01	1
		0.08 + 0.01	2
Monocrystal from avachita (Kamchatka)	89.7	0.08 + 0.03	1
Nodule of alkali basalt San Carlos (Arizona, USA)	91.1	0.017 + 0.008	1
Nodule from spinel + amphibole lherzolite (Baikal)		0.0003 + 0.0001	2
Nodule from garnet lherzolite		0.0012 + 0.0002	2
Nodule from spinel lherzolite (Mongolia)		0.0002	2
Nodule from spinel lherzolite (Mongolia)		0.0005 + 0.0001	2

equilibrium also increases (figure 5). The highest f_{O_2} values are characteristics of those xenoliths which show signs of cataclasis or which contain ilmanite. It may be concluded that the diamond-bearing peridotitic xenoliths from the upper mantle suffer a substantial change in the redox state.

Ideas about the f_{O_2} condition of equilibrium of diamond and chrome pyrope-bearing peridotites help to evaluate the composition of the fluid phase, which might have been in equilibrium with these rocks (figure 6). It is estimated that at a pressure of 50 kb and a temperature range of 1000 to 1300°C the fluid in equilibrium with diamond-bearing peridotites should have widely varying H_2O and CH_4 . The lowest f_{O_2} values are associated with fluids which are rather high in CH_4 (about 90–97 mol%). In the case of ultramafic rocks (diamond and chrome pyrope-bearing dunite and olivinite), the content of CH_4 sharply decreases, while that of H_2O increases. Cataclastic lherzolites, ilmenite and pyrope lherzolites were found to have equilibrated under f_{O_2} conditions where H_2O and CO_2 could coexist in equilibrium with the fluid.

The f_{O_2} condition of equilibrium of kimberlite sills is similar to that of cataclastic lherzolites (McMohan and Haggerty 1984; Haggerty 1986; Haggerty and Topkins 1985; Sobolev *et al* 1986).

The following is an attempt to generalize the experimental and thermodynamic data on the oxygen fugacity conditions involving mineral reactions at depth, which have been reported in numerous publications. Our observation regarding the redox state of lithosphere and the upper part of the atmosphere is illustrated in figure 7.

Figure 8 shows a similar generalization regarding the redox state of the region of formation of basic magmas in the mantle below the continents (stratified intrusive suites of Bushveld, Skaergaard, Stillwater, *etc.*), as well as the data on basalts of the oceanic floor. It follows from the diagram that the oxygen fugacity values of basaltic rocks correspond to the redox state of spinel lherzolites in the mantle below both the continents and the ocean. In general, magmatic melts show a gradual decrease in the oxygen fugacity values in the course of their ascent to the earth's surface.

Figure 5. Summary of intrinsic oxygen fugacity measurements for diamond-bearing peridotite (kimberlite tubes, Yakutia).

Figure 6. Composition of the fluid in equilibrium with diamond-bearing peridotite in the C-O-H system as a function of f_{O_2} at 50 kb and 1000°C (Kadik *et al* 1989). 1: diamond-bearing chrome-pyroxene herzburgite and ilmenite pyroxene ilmenite peridotites; 2: diamond-bearing dunite and sheared ilmenite pyroxene ilmenite peridotites; 3: diamond-bearing ilmenite pyroxene ilmenite peridotite, kimberlite.

Figure 7. Summary of redox state (calculated and experimentally determined) of peridotites from the upper mantle (based on various sources (see text).

Figure 8. Redox state of basaltic magmas: f_{O_2} for oceanic and island-arc basalts (Cristie and Carmichael 1986; Kadik and Zharkova 1990; Sato 1976), f_{O_2} for layered intrusive complexes of continental regions (Sato 1972; Sato and Valenza 1980; Ulmer *et al* 1987), f_{O_2} for lunar basalts (Sato 1976; Sato *et al* 1973).

Our conclusion regarding the redox state of the upper mantle below the continental areas is as follows:

The f_{O_2} values during different geochemical processes in the upper mantle vary broadly in the f_{O_2} -T space defined by the FMQ and IW buffers and the degree of variation is in four orders of magnitude. The upper mantle is largely heterogeneous as far as its redox state is considered. This is largely due to a number of chemical processes taking place within the mantle (e.g. melting, degassing, *etc.*). This conclusion is consistent with the ideas of many workers: Sobolev (1977); Arculus (1984); Haggerty (1986) and Green *et al* (1986), regarding the redox state of the lithospheric and asthenospheric layers of the upper mantle.

The f_{O_2} values determined for spinel peridotites differ considerably from those required for iron-silicate equilibrium. This means that the redox state of the upper part of the mantle has evolved considerably, compared to the early stage of mantle formation, when iron and nickel-bearing phases were in equilibrium.

The f_{O_2} values for diamond and chrome pyrope-bearing peridotites (classified as disintegrated rocks of ancient lithosphere) are rather low and correspond to those under which condition iron-silicate equilibrium takes place. This substantiates the view that the mantle is well reduced during the early stages of its evolution.

We may regard the increase in the oxygen potential as a basic tendency of the evolution undergone by the lithospheric and asthenospheric layers as far as their redox states are concerned. In some ways it is associated with the ascent of the mantle and the processes involving melting and degassing. This will be discussed further.

The areas of formation of kimberlite magmas in the mantle below the continents show dramatic changes in the redox state of the fluid regimes. From our experimental data we conclude that the melting process is preceeded by a considerable increase in the f_{O_2} condition of fluids which are in equilibrium with H_2O and CO_2 rather than CH_4 , the concentration of the latter being higher in its early stage of evolution.

The process of kimberlite magma formation appears to be associated with oxidation of the fluids at the upper part of the mantle, during which period, they became enriched in water and CO_2 . The temperature of peridotite melting during this stage shows a sharp decrease. This inference can be illustrated with the variation in the peridotite melting temperature as a function of the concentration of the fluid phase in equilibrium with graphite (figure 9).

Now let us discuss the factors which might bring about considerable changes in the redox state of the mantle particularly in the lithospheric-asthenospheric layers. This received worldwide interest (Eggler 1983; Arculus and Delano 1984; Haggerty and Topkins 1985; Kadik and Lukanin 1985, 1986; Green *et al* 1986; O'Neil and Wall 1987; Kadik 1988 and Mattioli *et al* 1990; Woermann and Rosenhauer 1985).

The process of melting and degassing of the mantle may be considered as the two most important factors. Many peculiarities in the redox state of the upper mantle are related to the physicochemical state of the early mantle.

If the mantle was subjected to a large-scale melting in a global scale, leading to the formation of large volumes of magma, differentiation of a magma and fractionation of the volatile components would lead to changes in its redox states. The presence of graphite could play a major role, if it is assumed that the composition of the mantle was similar to that of carbonaceous chondrites. The idea that the upper part of the earth's mantle may be similar to carbonaceous chondrite is believed to be true by many geo-scientists.

Figure 9. Effects of f_{O_2} on melting in the C-O-H-peridotite system at 20 kb and $C/(C+H)=1$ (Lukanin and Kadik 1987).

Our views concur with that of Green *et al* (1986) and Haggerty (1986). We consider that the CH_4 -rich fluid ascending from the lower mantle interact with the more oxidized material of the lithosphere. The question is – what are the peculiarities associated with the fractionation of volatile components in the course of evolution of the layer undergoing global melting particularly if graphite was present in the parent material?

In the presence of a graphite phase, the content of such volatiles as CO_2 , CO , CH_4 and H_2O should be largely controlled by the presence of a fluid phase (figure 10). Due to interaction between the graphite and the volatile components, species typical of reduced states such as CO , CH_4 and H_2O should be predominant in the upper part of the melt layer, while the deeper part of the liquid layer should be associated with H_2O and CO_2 . Because of contrasting compositional variation of the volatile composition, an intensive mass transfer would take place during the convective movement of the melt. The process should involve a generation of more oxidized melts and inflow of material from the deeper part of the liquid layer into the more reduced layers found near surface. This would inevitably result in the burning-out of graphite and oxidation of the melt in general.

Thus the condition of intensive convection and mass transfer favour the process of self-cleaning of the melt zone with respect to graphite. Simultaneously, the total oxygen potential of the system increases and the content of oxidized species of carbon becomes higher (see figure 10).

At the same time there are reasons to believe that in the top section of the upper mantle, there are layers with higher oxygen potential, compared to the deeper layers of the mantle. Subsequent process related to the melting of the upper mantle material should also result in increasing the f_{O_2} condition of the deep-seated layers.

If our contention is correct, the deeper part of the mantle which avoided melting

Figure 10. Outgassing in convecting magma layer (magma ocean) at the planetary surface (A) and supposed changes in f_{O_2} with height in presence of graphite, scheme showing increasing trends of f_{O_2} in magma layer during outgassing and graphite burning (J_1, J_2, J_3) and dissipation of H_2 (B).

at an earlier or later stage of earth's evolution probably has preserved more reduced states. These layers might be responsible for supplying fluids under highly reduced conditions to the lithospheric-asthenospheric layers of the upper mantle.

In the case of kimberlite magmas, there is a dramatic change in the composition of the fluid. It probably contains CH_4 at an early stage, but are in equilibrium with H_2O and CO_2 at a later stage. Rather low values of f_{O_2} estimated for some samples of spinel lherzolites and continental and oceanic basalts suggest that even in these cases, magmatism was associated with mass transfer of fluids from the lower part of the mantle. However this conclusion warrants further discussion.

Thus we may conclude that the upper mantle is profiled with respect to its redox state, oxidized in the upper part (lithospheric and asthenospheric layers), but reduced in the deeper part (below the region of magma formation). This is in agreement in most aspects with the models proposed by Haggerty (1986). However, the main trend of evolution of the mantle involves oxidation in general.

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