

Geochemical history of the convecting upper mantle: A comparison of ophiolites

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I. Introduction

The convecting upper mantle is the primary source of mid-ocean ridge basalts from which much of the continental crust is ultimately derived (Winter, 2010). Convection in the upper mantle drives plate tectonics, the unifying theory of terrestrial geology. Despite the importance of the convecting upper mantle, its chemical evolution remains poorly understood. Techniques which can be used to examine long term chemical evolution in the convecting upper mantle are now well developed. Processes such as melting in the convecting upper mantle leave specific geochemical signatures, including depletions or enrichments in certain elements or isotopes. By studying the geochemical changes in the convecting upper mantle, the evolution of melting and other processes can be better determined.

A suite of transition metals called the highly siderophile elements (HSE) are a major focus of study for investigating current and past processes in the Earth's mantle. As their name suggests, the HSE (including Os, Ir, Ru, Pt, Pd, and Re) are chemically stable in iron alloys because of properties like valence state and ionic radius (Meisel, 2008). Given this, it might be expected that the HSE would almost entirely reside in the Earth's metallic core. However, in the mantle they are found in concentrations only about 200 times less than in chondrites. Multiple hypotheses have been generated to explain the relatively high abundance of HSE in the mantle (Morgan, 1986; Richter, 2008; Brandon and Walker, 2005). Regardless of the reason, the HSE provide important information about long-term geochemical processes occurring in the Earth's largest silicate reservoir (Rudnick and Walker, 2002).

This project seeks to define the secular geochemical evolution of the convecting upper mantle, specifically by examining changes in the nature of melting and metasomatism, utilizing the HSE. These petrologic processes have significant control over the geochemistry of the convecting upper mantle through the removal and addition of mobile elements. To better understand evolution of melting and metasomatism in the convecting upper mantle, abundances of HSE in peridotites from ophiolites with ages ranging from 6 Ma to 1950 Ma are examined and compared.

Ophiolites are stratified rock sections comprised of layers of deep ocean sediment, basalt pillows and dikes, gabbro and peridotitic mantle. Because of the inclusion of ultramafic rocks and the mid-ocean ridge basalt (MORB) character of some ophiolitic basalts, ophiolites are theorized to be sections of uplifted oceanic crust and underlying mantle (Dilek and Furnes, 2011). Ophiolitic peridotites are typically depleted in incompatible trace elements, including the light rare earth elements, and have high concentrations of MgO. These geochemical signatures lead to the presumption that these rocks represent the uppermost portion of the convecting upper mantle (Dilek and Furnes, 2011). Because my project studies the evolution of the convecting upper mantle, I have focused on geochemical analysis of the peridotitic portions of the ophiolites. Harzburgites, lherzolites and dunites (Fig. 1) are the dominant lithologies typically found in the ultramafic portions of ophiolites. In most cases, these rocks are strongly serpentinized.

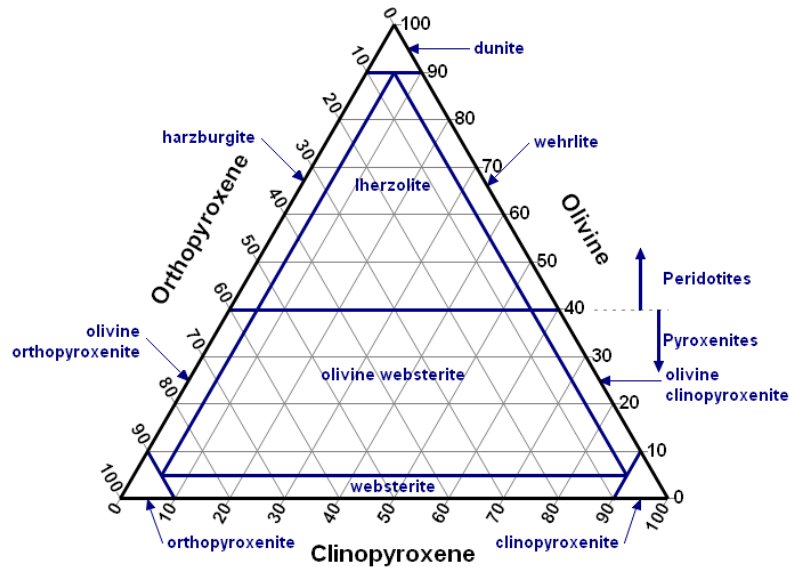


Figure 1. Plot shows the petrologic definition of ultramafic rocks examined in this project (from Winter, 2010).

The ophiolites I have studied in this project are of two major types: mid-ocean ridge (MOR) type and supra-subduction zone (SSZ) type. MOR ophiolites are formed at mid-ocean ridges and are typically depleted in elements that are incompatible in mantle minerals. However, their geochemistry can be enriched in these elements by direct interactions with continental crust or indirectly, through interaction with crustally-derived fluid. SSZ ophiolites are formed from the plate which is not subducted at a subduction zone, during the closure of an oceanic basin (Dilek and Furnes, 2011). SSZ ophiolites are generally more enriched in incompatible trace elements compared to the MOR type. While I analyzed both SSZ and MOR ophiolites, I focused on MOR type because they more closely resemble the convecting upper mantle (Dilek and Furnes, 2011; Schulte et. al, 2009).

The isotopic compositions of Os and the concentrations of the HSE have been compared in peridotites from the different aged ophiolites to better understand the geochemical evolution of the upper convecting mantle. ^{187}Re decays to ^{187}Os by beta decay with a 41.6 billion year half-life (decay constant $\lambda=1.66\text{E}-10$).

The difference in geochemical characteristics between Re and Os make this an ideal decay suite to determine the timing and magnitude of an ancient melting event. Rhenium is incompatible in most mantle minerals and is almost completely removed from the residue with small to moderate amounts of partial melting (Shirey and Walker, 1998). Osmium is compatible in non-silicate mantle minerals like sulfides and intergranular metal alloys (Walker et. al, 2005). A melting event in a mantle reservoir's history tends to remove Re from the residue and, over long time scales, retards the growth of the $^{187}\text{Os}/^{188}\text{Os}$ of a rock compared to ambient, undepleted mantle (Shirey and Walker, 1998). For example, the $^{187}\text{Os}/^{188}\text{Os}$ of the mantle during the Phanerozoic may be governed by a melting event that took place in the Proterozoic. Similarly, depletion in the $^{187}\text{Os}/^{188}\text{Os}$ of the Proterozoic mantle may have been governed by melting that occurred in the Archean.

To determine the Os isotopic composition at the time the ophiolite formed, referred to as a time normalized isotopic composition, the ophiolite's crystallization age must be known (Snow et. al, 2000). Time normalized $^{187}\text{Os}/^{188}\text{Os}$ can be calculated for the age of an ophiolite using the equation:

$$^{187}\text{Os}/^{188}\text{Os}_i = ^{187}\text{Os}/^{188}\text{Os}_* - ^{187}\text{Re}/^{188}\text{Os} (e^{\lambda t} - 1)$$

Equation 1 The decay equation is used to calculate time-normalized $^{187}\text{Os}/^{188}\text{Os}$. $^{187}\text{Os}/^{188}\text{Os}_*$ is the present ratio measured.

$$\gamma\text{Os} = \left(\frac{^{187}\text{Os}/^{188}\text{Os}_{\text{sample}}(t)}{^{187}\text{Os}/^{188}\text{Os}_{\text{chondrite}}(t)} - 1 \right) * 100$$

Equation 2 The γOs notation is used to compare time-normalized Os isotopic compositions. γOs is the deviation of a sample's $^{187}\text{Os}/^{188}\text{Os}$ to the chondritic ratio at a given time. The chondritic ratio is calculated using Eq. 1 solar system initial $^{187}\text{Os}/^{188}\text{Os} = 0.09531$ and $^{187}\text{Re}/^{188}\text{Os} = 0.40186$.

The measured $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ of ophiolite samples are used to calculate the time normalized Os isotopic composition at the crystallization age (Eq. 1). In this study, ophiolite formation ages are taken from previous work on the ophiolite using other geochronometers. The time normalized Os isotopic composition in an ophiolite can be compared to a model mantle evolution curve to determine the extent of long-term Re depletion by mantle melting. In this project, Os isotopic compositions were compared based on γOs values. γOs is the percent deviation from the chondritic Os composition at the time a rock crystallized (Eq. 2)

Analysis of the concentrations of HSE can be studied to illuminate incompatible element depletion and metasomatic geochemical processes affecting the convecting upper mantle. Osmium, Ir and Ru are generally compatible in mantle minerals, and so are concentrated in the upper convecting mantle when it undergoes partial melting (Rudnick and Walker, 2002). Platinum is typically less compatible than Os, Ir and Ru, but can still be found in relatively high concentrations in mantle rocks. Palladium and Re are generally incompatible in most mantle minerals and tend to partition strongly into mantle-derived melts. Therefore, they are normally found in lower concentrations in ultramafic rocks that have undergone prior melting (Meisel, 2008). Dunites are an exception to this rule because they are peridotites which can form from a mafic melt by crystal-liquid fractionation. Dunites are rocks where olivine comprises greater than 90 percent of the rock's mass (Fig. 1). During crystal-liquid fractionation, olivine crystals can be chemically separated from the melt to form dunites. Mantle-derived melts from which dunites form are commonly enriched in incompatible HSE and depleted in compatible HSE. If the dunite is chemically separated from the melt, the incompatible HSE will remain in a greater concentration than in other peridotites (Buchl et. al, 2002).

In peridotites, variability in relative concentrations among the HSE is used to study their melting and metasomatic history. In a mantle reservoir where melt removal was the dominant geochemical process, concentrations of the incompatible HSE, when normalized to chondrites or

the primitive upper mantle (PUM), will be depleted compared to fertile mantle. Metasomatism, the addition of chemical components to a rock by a foreign liquid, is another process affecting the geochemistry of the convecting upper mantle. If metasomatism is the dominant process, the incompatible HSE will approach or exceed PUM-normalized concentrations (Rudnick and Walker, 2009). This is because the liquids involved in convecting upper mantle metasomatism are generally mantle-derived melt, which is concentrated in the incompatible HSE.

II. Geological Context

The ophiolites I have analyzed in this project come from various locations and were formed at different times. The ages of the ophiolites roughly corresponds to the age of the mantle melting that formed them. Therefore the different ophiolite suites that I will be comparing represent the mantle at different times in Earth history.

1. Jormua Ophiolite (1.95 Ga)

The oldest ophiolite I analyzed for this project is the Jormua ophiolite in northern Finland (Fig. 2). It trends east-west and is composed of three separate units. U-Pb dating of zircons in the gabbroic dikes associated with the ophiolite indicates a 1.95 Ga formation age (Peltonen et. al, 1998). Previous studies have determined the Os isotopic composition of Jormua peridotites (Tsuru et. al, 2000), but measurement techniques of Re have since been improved and a present day measurement will yield more accurate Re/Os ratios. HSE concentrations have not previously been determined for peridotites from this ophiolite.

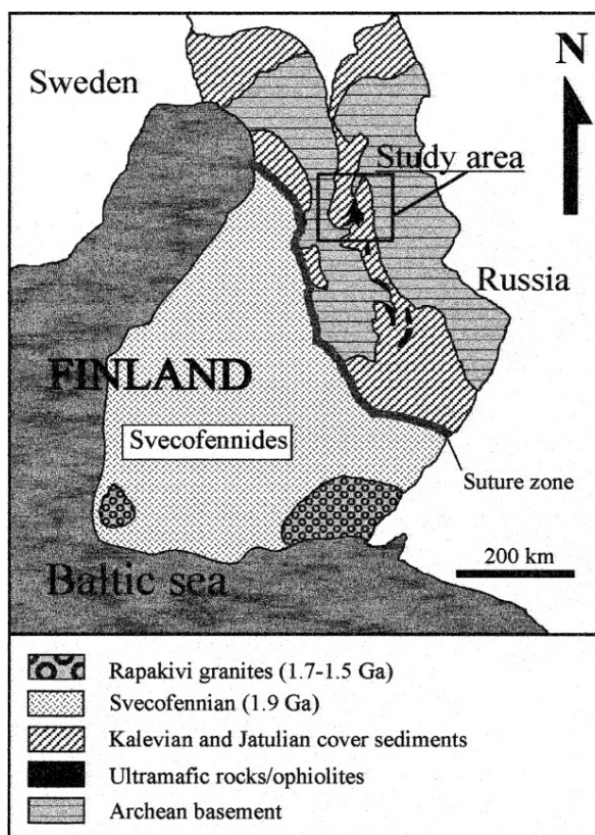


Figure 2 Map shows the location of the Jormua ophiolite in Finland (from Tsuru et. al, 2000)

This ophiolite has been characterized as being mostly of MOR origin (Peltonen et. al, 1998). The serpentinites of the Antinmaki unit showed great variability in Re/Os in previous research, which may be suggestive of open system behavior (Tsuru et. al, 2000). Tsuru et. al 2000 separated oxide and chromite minerals from whole rocks for analysis but my project focused on whole rock isotopic composition and HSE concentrations. I have analyzed 10 Jormua peridotite samples: 8 from Antinmaki and 2 from the Lehmivaara block (Fig. 3).

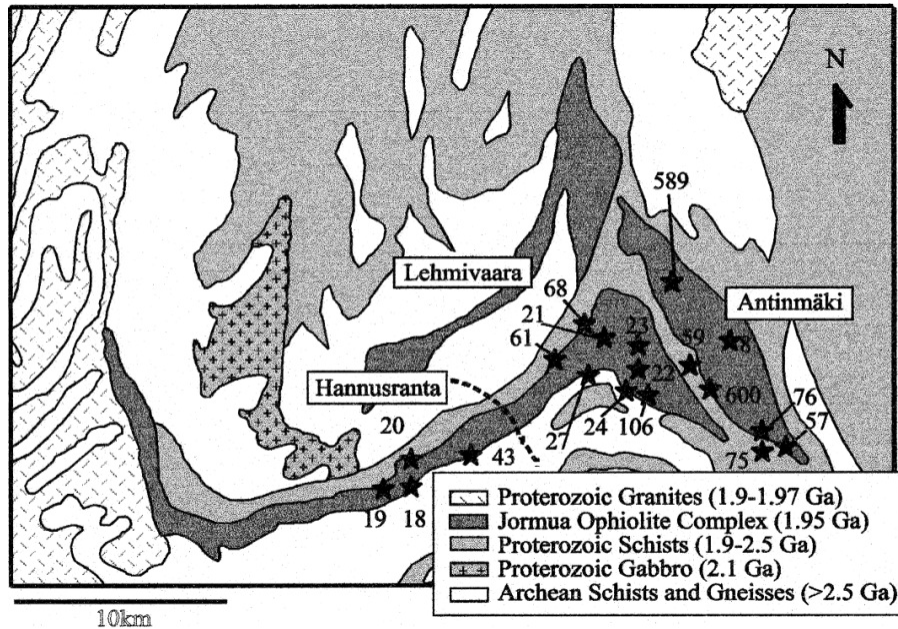


Figure 3 Geologic map shows the units of the Jormua ophiolite (Tsuru et. al, 2000)

2. The Albanian Ophiolite (0.165 Ga)

The Albanian ophiolite covers the length of Albania with a general NNW-SSE trend (Hoek et. al, 2002). It is part of a chain of ophiolites that stretches from Spain through southern Europe and the Middle East to the Himalayas (Dilek and Furnes, 2011). Its age was previously determined to be 161-173 Ma using $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the metamorphic region created by the emplacement of the ophiolite (Marccuci and Praela, 1996). In Albania, this ophiolite consists of a western and eastern chain with differing lithologies, distribution and size, and geochemical signature (Fig. 4a). The ultramafic rocks found in the western chain are typically harzburgites and lherzolites, as well as plagioclase-bearing lherzolites and dunites. Harzburgites, dunites and pyroxenites are found in the eastern chain. The western chain covers a greater area but is only 2-3 km thick compared to thicknesses of 6-10 km found in the eastern ophiolite chain (Hoeck et. al, 2002).

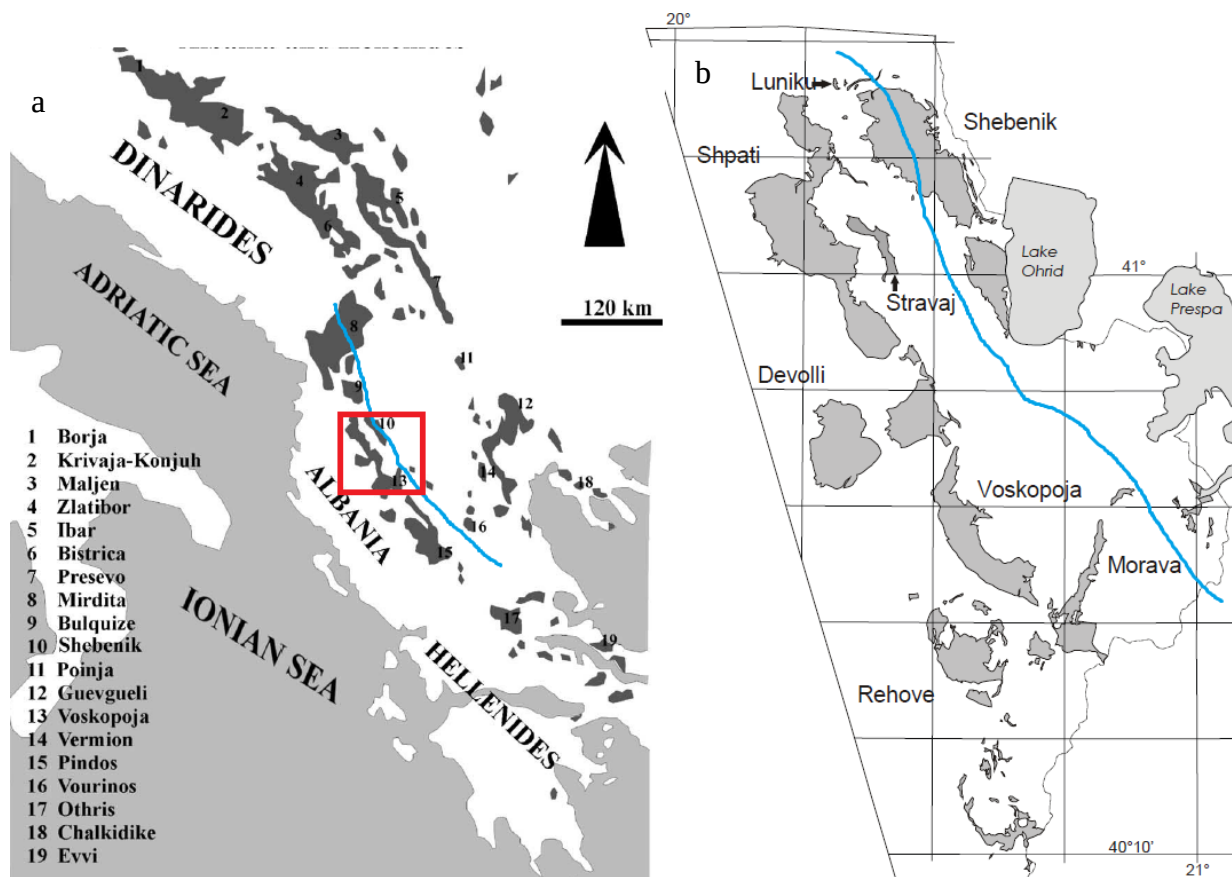


Figure 4 (a) Regional map shows the location of the Albanian ophiolite in southern Europe and the blue line is the boundary of the eastern and western ophiolite chains (from Hoeck et. al, 2002). (b) Sketch of the Albanian ophiolite units sampled in this study in greater detail (from Meisel, 2005).

The presence of boninite dikes, rocks with high MgO and SiO₂ content, at subduction zones, and a relative enrichment of the light rare earth elements suggests a SSZ type origin for the eastern ophiolite chain (Hoeck et. al, 2002). The Mirdita and Shebenik units of the Albanian ophiolite are complex configurations of both SSZ and MOR ophiolites and cannot be grouped into the eastern or western chain (Fig. 4).

Most of the samples I analyzed for this project are from the western MOR ophiolite chain, but some are from the Shebenik and Mirdita units which have complex interlayering of rocks representing the eastern and western chains. This allows comparison of HSE systematics of MOR-type and SSZ-type peridotites from the same general ophiolite. I have analyzed 16 Albanian peridotites: two from Shebenik, three from Shpati, three from Devolli, one from Luniku and seven from Bulqize.

3. Taitao Ophiolite (0.006 Ga)

The Taitao ophiolite is located in Chile along the Pacific coast on the Taitao peninsula (Fig. 5a). U-Pb dating of zircons in the gabbroic layer of the ophiolite yields a 6 Ma age. This indicates that the Taitao ophiolite was likely generated by ridge collision and subduction in the Pacific Ocean (Anma et. al, 2009). Work by Shibuya et. al, 2007 determined that Taitao is a

MOR ophiolite. The Os isotopic composition of the Taitao ophiolite is typical of abyssal peridotites and the depleted MORB mantle (DMM). Schulte et. al (2009) interpreted the measured Os isotopic composition as indicative of Re/Os fractionation by a melting event at 1.6 Ga. Some peridotites show relatively high concentrations of the incompatible HSE, suggesting recent metasomatism.

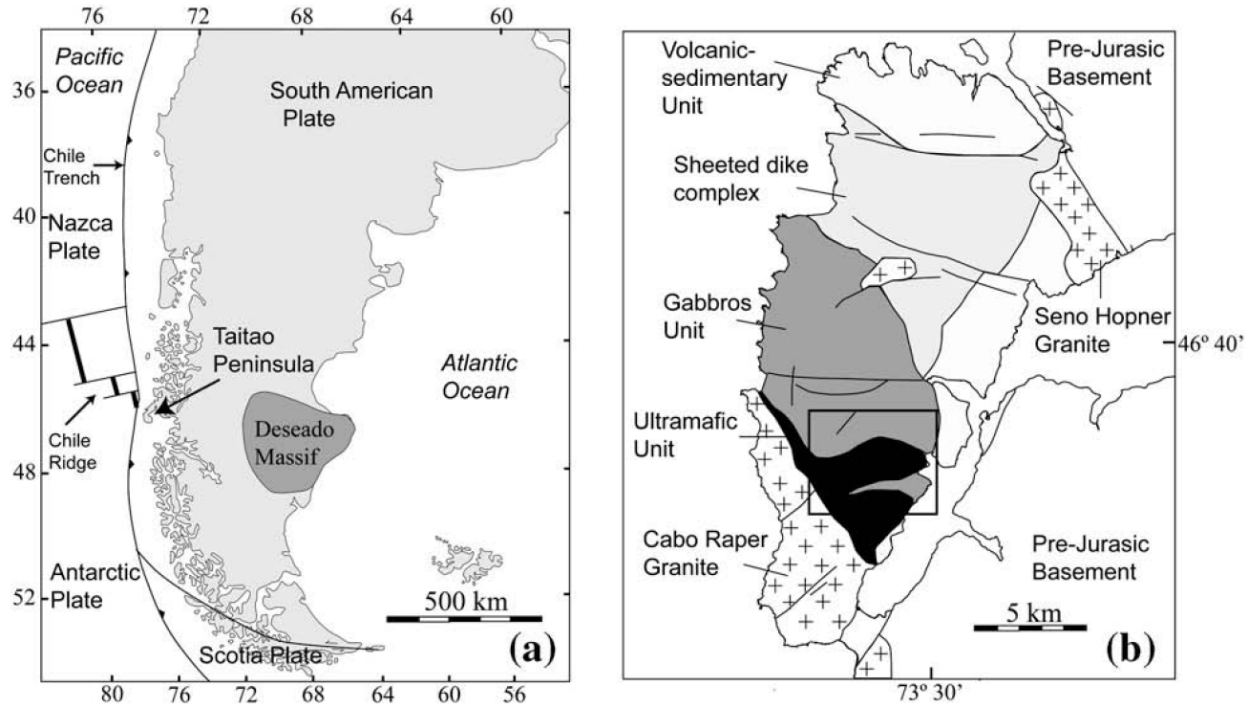


Figure 5 (a) Map shows the location of the Taitao ophiolite in Chile. (b) Geologic map shows the lithologies of the ophiolite and associated formations (from Schulte et. al 2009)

III. Methodology

To determine Os isotopic compositions and HSE concentrations for ultramafic rocks from the Albanian and Jormua ophiolite, isotopic ratios were measured on the mass spectrometer.

In order to prepare a sample for mass spectrometry, the elements being measured were separated from each other in order to avoid isobaric interference. Isobars are two isotopes of different elements that have the same mass. If an isobar is present in solution when the isotopic ratio is being measured, the ratio will not be correct because it will include the isobar.

The first step in chemical separation of the HSE is acid digestion. Around 2 g of a sample powder is placed in a Carius tube with 9 mL of a 2:1 mixture of HNO_3 and HCl . This mixture is baked at 235°C so the acid mixture can dissolve HSE-bearing alloys in the sample, leaving behind a silica slurry. Osmium is then removed from the acid by addition of CCl_4 . Osmium is in a 8+ oxidized state and will partition into CCl_4 . Immiscibility and density difference allow the osmium to be simply extracted from the other HSE. Os is then reduced by addition of HBr and purified by a process known as microdistillation. During microdistillation, dichromate oxidizes Os to its most oxidized state. In this state, Os is extremely volatile and will travel through air to a

small drop of HBr. To separate the HSE other than Os, an anion exchange column is used. Rock components other than the HSE will wash through the column while the HSE will remain only until interaction with highly concentrated HNO_3 and HCl (Shirey and Walker, 1995).

The current $^{187}\text{Os}/^{188}\text{Os}$ of a rock can be measured by negative thermal ionization mass spectrometry (N-TIMS). Other HSE isotope ratios are measured on an inductively coupled plasma mass spectrometer (ICP-MS). For this study Os ratios are measured on the NBS Bobcat and VG Sector 54 N-TIMS at the University of Maryland, College Park and HSE ratios are measured on the Nu ICP-MS.

HSE concentrations were calculated using the isotope dilution method. In this method a solution with a known isotopic composition is added to a sample. This solution, called a “spike,” is highly concentrated in an isotope which will be measured by mass spectrometry. When the isotopic ratio of the sample-spike mix is measured, the isotopic ratio of the sample can be calculated because the researcher will know how much of the atoms of each isotope are from the spike.

There are several sources of error in elemental concentrations and isotopic compositions measured by the methods described. Gross errors in chemical separation are minimized by meticulous cleaning of laboratory equipment and observation of clean lab procedures. Poisson’s counting statistics are applied to determine a standard deviation of each isotopic ratio measured mass spectrometry. 2σ uncertainties in isotope ratios measured by mass spectrometry are normally around 0.1%. Instrumental drift is quantified by the deviation from the natural isotopic composition of a standard’s measured isotopic composition. The percent deviation of the measured value from the accepted standard is used for fractionation correction of measured isotopic ratios. This deviation is typically around 0.1%, and is considered a minor source of error for most measurements.

Blank correction is made by simply subtracting the measured amount of an element in the blank from the measured amount of the element in the sample. It may provide a minor or major source of error, depending on the HSE in question. More concentrated elements will require only slight correction, even with high blanks. However, Re is found in very low concentrations in peridotites, so the blank Re may make up a significant amount of Re measured. For the samples from the Albanian ophiolite, two different blanks were used. The first blank had 2.68 pg Re (0.5-4% of total Re), 6.58 pg Os (0.07-0.12% of total Os), 34.2 pg Ir (0.42-0.57% of total Ir), 42.4 pg Ru (0.25-0.46% of total Ru), 81.1 pg Pt (0.35-0.75% of total Pt) and 53.0 pg Pd (0.09-0.46% total Pd). The second blank had 13.2 pg Re (1-10% of total Re), 4.52 pg Os (0.04-0.09% of total Os), 19.1 pg Ir (0.20-0.66% of total Ir), 227 pg Ru (1.17-3.61% of total Ru), 83.69 pg Pt (0.38-0.48% of total Pt) and 155 pg Pd (0.48-0.95% of total Pd). One blank was used for the samples from the Jormua ophiolite with 2.43 pg Re (1-4% of total Re), 4.95 pg Os (0.02-0.11% of total Os) 7.62 pg Ir (0.07-0.11% of total Ir), 780 pg Ru (4-19% of total Ru), 67 pg Pt (0.43-3.14% of total Pt) and 51.2 pg Pd (0.65-8.77% of total Pd).

Adding too much or too little of a spike solution can also cause error magnification. Error propagation of these sources of uncertainty typically produces 2σ ranging from 0.1% to 1%. More abundant HSE will have lower uncertainty, while the least abundant, Re, could have a 1-5% 2σ standard deviation. In this project, Re concentrations have an average of 3% 2σ standard deviation with a range of 1-4%. Os concentrations have an average of 1.1% 2σ standard

deviation. Average 2σ standard deviation for the other HSE are: 1.0% for Ir, 1.3% for Ru, 1.5% for Pt, and 1.1% for Pd.

IV. Hypotheses

There are three hypotheses which were tested by this study. They all are consequences of growing heterogeneity in the mantle through time. They are based on the idea that an older ophiolite preserves the young, less differentiated mantle.

1. Distribution of Osmium Isotopic Composition

I hypothesize there will be a greater variance of γOs values in the Phanerozoic mantle compared to the Proterozoic mantle (Eq. 1). Younger mantle experienced more partial melting, fractionating incompatible HSE from compatible HSE and resulting in greater heterogeneity. As time progresses, melting and metasomatic processes accumulate and increase Os isotopic heterogeneity.

The corresponding null hypothesis is that there will be no difference in the variance of γOs values in the Phanerozoic mantle compared to the Proterozoic mantle.

2. Average Osmium Isotopic Composition

I hypothesize that the γOs values of the Albanian and Taitao ophiolites will average lower than the Jormua ophiolite. Repeated removal of ^{187}Re increasingly retards the growth of ^{187}Os over time. Therefore, the Os isotopic composition of the Jormua at 1.95 Ga would be lower than the Os isotopic composition of the Albanian ophiolite at 0.165 Ga and the Taitao ophiolite at 0.006 Ga. A lower isotopic composition would deviate more greatly from the chondritic ratio at the time of crystallization.

The null hypothesis is that γOs will average the same for ancient and modern mantle.

3. Highly Siderophile Element Concentration

I hypothesize that the PUM-normalized HSE concentrations of the Phanerozoic mantle will be more variable than that of the Proterozoic mantle. The difference between normalized incompatible HSE concentration and normalized compatible HSE concentration in the Albanian and Taitao ophiolites will be greater than the difference between normalized incompatible and compatible HSE in the Jormua ophiolite. Repeated melting and metasomatic events would have increased the difference between normalized incompatible and compatible HSE concentration.

The corresponding null hypothesis is that there will be no variability between incompatible and compatible HSE in the ancient mantle compared to modern mantle.

V. Results

Table 1 HSE concentration and Os isotopic data including Re-depletion age (T for Albanian ophiolite. Initial ratios are age-corrected for 0.165 Ga.

	Re(ppb)	Os(ppb)	Ir(ppb)	Ru(ppb)	Pt(ppb)	Pd(ppb)	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	initial $^{187}\text{Os}/^{188}\text{Os}$	γOs
A02/287	0.1620	3.176	2.827	5.631	6.973	13.047	0.1241(3)	0.2354(11)	0.1235(34)	-1.9(0)
A06/710	0.3508	3.922	3.652	7.671	8.831	11.077	0.1282(3)	0.4130(31)	0.1271(33)	0.96(3)
A08/825	0.0327	2.678	4.071	4.378	6.064	28.405	0.1186(3)	0.0563(1)	0.1185(33)	-5.9(2)
A06/734	0.2843	3.975	3.466	7.592	7.128	13.804	0.1250(3)	0.3301(21)	0.1242(34)	-1.4(0)
A05/541	0.0327	4.975	3.790	8.204	10.44	12.404	0.1277(3)	0.0303(1)	0.1277(31)	1.4(0)
A09/920	0.0110	3.591	3.019	6.812	5.631	6.411	0.1197(3)	0.0142(2)	0.1197(35)	-4.9(1)
A06/727	0.0500	4.172	3.790	7.720	5.369	5.657	0.1185(3)	0.0552(1)	0.1184(31)	-6.0(2)
A10/1000	0.0595	4.315	3.019	7.912	10.52	13.100	0.1265(3)	0.0637(1)	0.1264(36)	0.4(0)
A02/286	0.7448	2.573	1.399	2.962	9.868	15.562	0.1351(1)	1.3378(82)	0.1315(8)	4.4(0)
A06/730	0.2669	3.319	2.986	6.459	9.260	9.151	0.1265(1)	0.3713(5)	0.1255(7)	-0.29(0)
A08/792	0.1122	5.510	4.590	9.426	10.88	8.620	0.1218(3)	0.0940(2)	0.1216(35)	-3.4(1)
A10/1001	0.0734	5.023	4.286	9.423	10.41	9.890	0.1260(1)	0.0674(1)	0.1259(6)	0 (0)
A08/822	0.1077	6.150	2.819	4.881	9.497	8.084	0.1250(1)	0.0808(1)	0.1249(8)	-0.8(0)
A10/1004	0.2374	4.404	4.238	8.993	10.97	10.253	0.1400(4)	0.2493(14)	0.1394(44)	10.7(3)
A05/563	0.2682	3.895	3.234	7.083	8.627	8.817	0.1150(48)	0.3173(362)	0.1142(580)	-9.3(4.7)
A06/680	0.3163	3.502	2.115	6.657	9.956	11.426	0.1304(1)	0.41710(1)	0.1293(10)	2.7(0)

Table 2 HSE concentrations and Os isotopic data for Jormua ophiolite. Initial ratios are age-corrected for 1.95 Ga.

	Re(ppb)	Os(ppb)	Ir (ppb)	Ru(ppb)	Pt (ppb)	Pd(ppb)	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	initial $^{187}\text{Os}/^{188}\text{Os}$	γOs
ATK57-A	0.034	3.254	4.456	5.689	7.718	3.844	0.1159(2)	0.0504(5)	0.1142(12)	0.45(1)
ATK57-B	0.037	4.037	3.544	7.517	4.738	3.015	0.1157(2)	0.0436(4)	0.1143(12)	0.46(1)
ATK59	0.112	2.665	2.386	5.065	3.877	2.341	0.1174(2)	0.2028(20)	0.1107(11)	-2.7(0)
ATK75	0.033	4.820	3.877	9.206	4.456	1.842	0.1115(2)	0.0329(3)	0.1104(11)	-2.9(0)
ATK76	0.052	6.159	4.422	1.656	4.976	1.120	0.1113(2)	0.0404(4)	0.1100(11)	-3.3(0)
ATK96	0.284	3.457	3.020	7.451	6.037	3.105	0.1146(2)	0.3952(40)	0.1016(10)	-10.7(1)
ATK589	0.030	10.84	5.605	9.336	6.715	2.575	0.1111(2)	0.0135(1)	0.1107(11)	-2.7(0)
ATK600	0.046	3.623	1.815	4.052	3.587	2.071	0.1176(2)	0.0605(6)	0.1156(12)	1.6(0)
LHV21	0.084	2.206	0.364	2.646	3.013	0.916	0.1174(2)	0.1835(18)	0.1113(11)	-2.1(0)

I have measured Os isotopic composition and HSE concentrations for 16 samples from the Albanian ophiolite and 10 samples from the Jormua ophiolite.

Osmium isotopic compositions of the Albanian ophiolite are typical for the DMM and the average $^{187}\text{Os}/^{188}\text{Os}$ of 0.12557 is less than 0.5% greater than the average for modern abyssal

peridotites, 0.125 (Becker et. al, 2006). The average initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.12486 was not greatly affected by the 0.165 Ga age corrections (Table 1). As a point of comparison, the average initial $^{187}\text{Os}/^{188}\text{Os}$ of the Taitao ophiolite is 0.12411.

The average initial Os isotopic composition of the Jormua ophiolite is 0.1122, lower than values measured for the modern DMM (Becker et. al, 2006). An internal check of the chemical methods and mass spectrometry used in this project was performed by running sample ATK57 through the digestion, distillation and column chromatography steps two separate times and measuring its elemental concentrations and Os isotopic composition. Concentrations of Ir and Pt of ATK57-A and ATK57-B differ, suggesting some kind of interference in the measurement of one of these elements on ICP-MS. The measured $^{187}\text{Os}/^{188}\text{Os}$ of ATK57-A and ATK57-B are very similar, suggesting confidence in the performance of the TIMS used in this project.

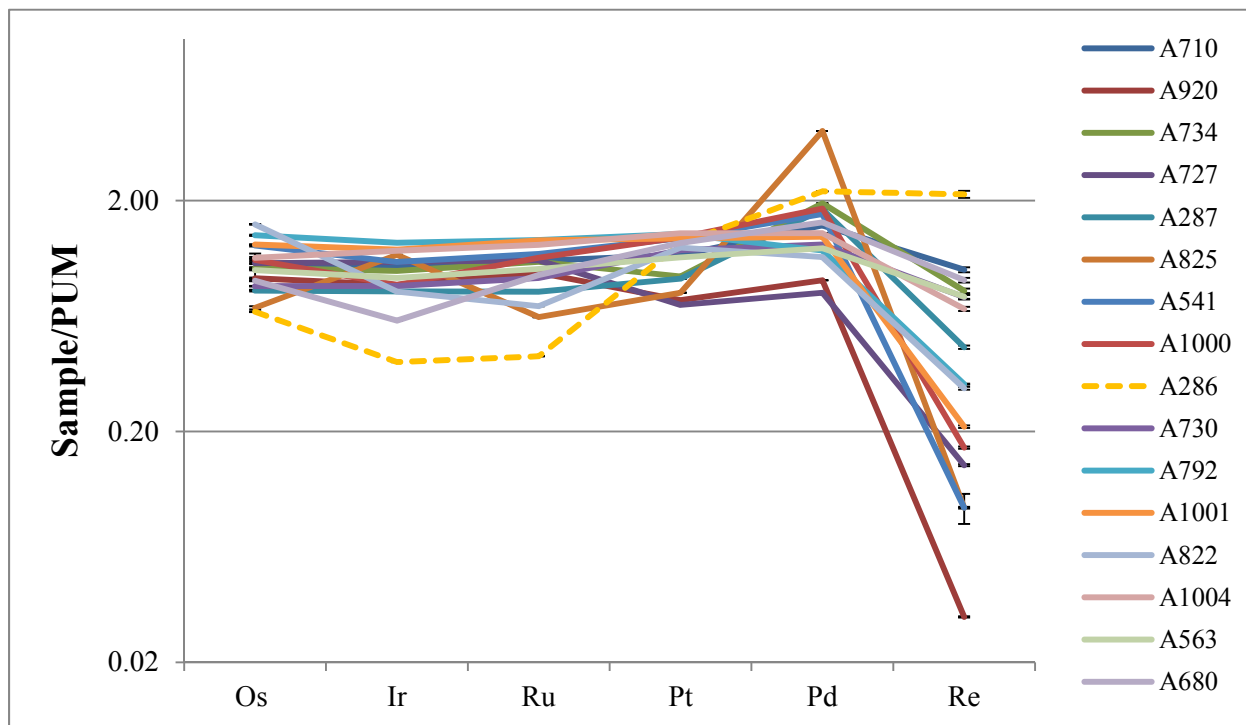


Figure 6 Plot shows HSE concentrations of Albanian harzburgites and lherzolites normalized to PUM (values from Becker et. al, 2006). A286, a dunite, is indicated by the dashed line.

The concentrations of the HSE were analyzed to determine the extent of metasomatism, partial melting and melt removal, and convective mixing before an ultramafic rock in an ophiolite crystallized. If the incompatible HSE are relatively depleted compared to the compatible HSE, melt removal was likely dominant. If the concentrations of incompatible HSE are relatively enriched compared to the compatible HSE, metasomatism may have added the incompatible elements.

The HSE concentrations for the Albanian ophiolite are variable; some samples resembled the PUM, while others represent the modern DMM (Becker et. al, 2006; Schulte et. al, 2009). PUM normalization shows deviation from the homogenous mantle's composition.

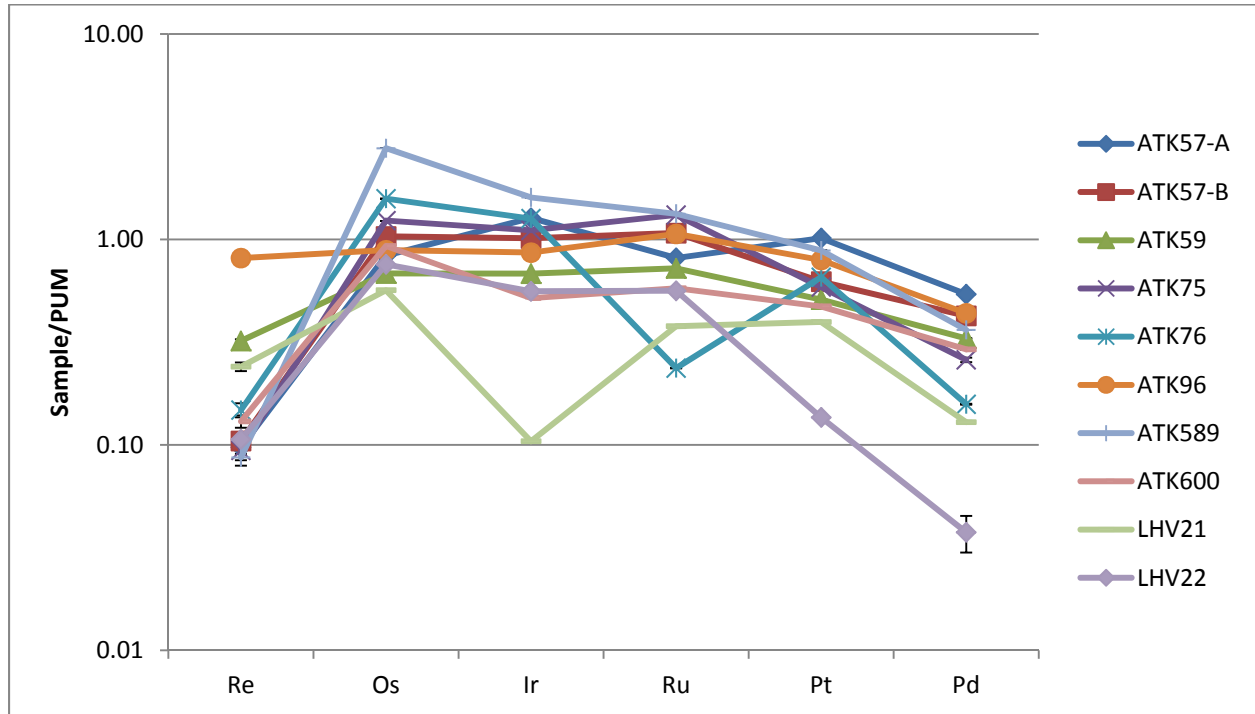


Figure 7 Plot shows HSE concentrations of Jormua harzburgites and lherzolites normalized to PUM (values from Becker et. al, 2006).

Most Jormua peridotites are strongly depleted in incompatible HSE (Re, Pt, Pd). However, some are also depleted in compatible HSE. Samples from the Lehmivaara, LHV21 and LHV 22, have unique concentrations for some HSE. LHV21 is the only sample depleted in Ir relative to PUM and LHV22 shows extreme depletion in incompatible HSE.

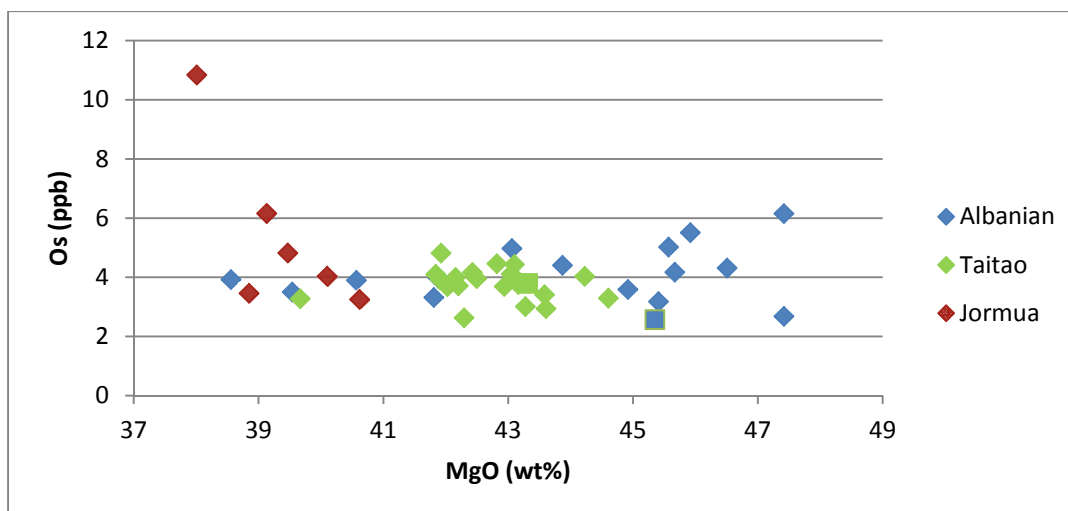


Figure 8 Plot shows MgO and Os concentration. Dunites are indicated by square symbols, other peridotites are symbolized by diamonds.

Major element data for the Albanian ophiolite is provided by Thomas Meisel (unpublished). Major element data for the Taitao ophiolite is from Schulte et. al, 2009. Typical major element data for the Antinmaki and Lehmivaara blocks of the Jormua ophiolite is taken from Peltonen et. al, 1998 and is plotted against Os concentration of ATK57-A, ATK76, ATK96 and ATK600 of the Antinmaki block and LHV21 and LHV22 of the Lehmivaara block. Most Jormua samples have similar MgO concentrations, but are depleted in Os relative to younger ophiolites (Figure 8).

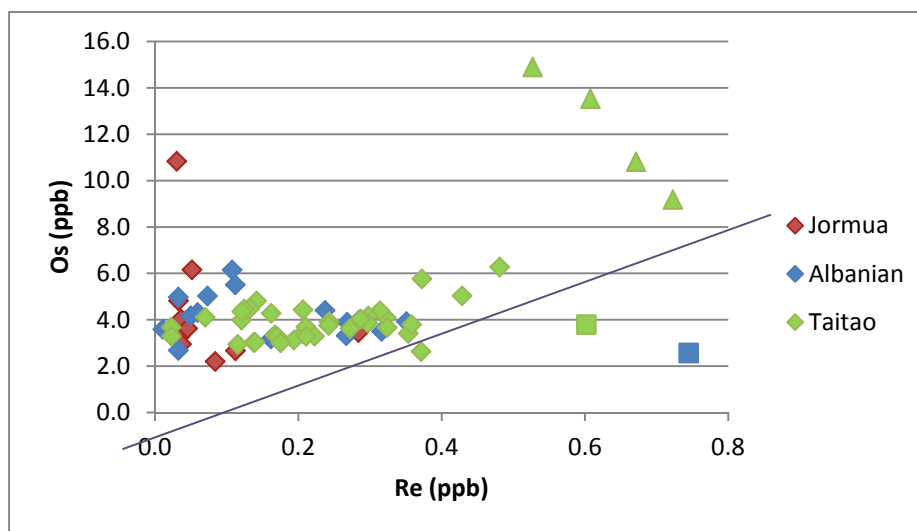


Figure 9 Plot shows Os and Re concentrations (ppb). Average Os/Re for Earth's upper mantle from Becker et. al, 2006 are indicated by the purple line Dunites are indicated by square markers, other peridotites are symbolized by diamonds and triangles represent chromite mineral separates.

Os/Re of most peridotites from all ophiolites analyzed in this project is greater than that of the PUM (Becker et. al, 2006). The Jormua ophiolite is depleted in Re compared to the Taitao and some samples from the Albanian ophiolite.

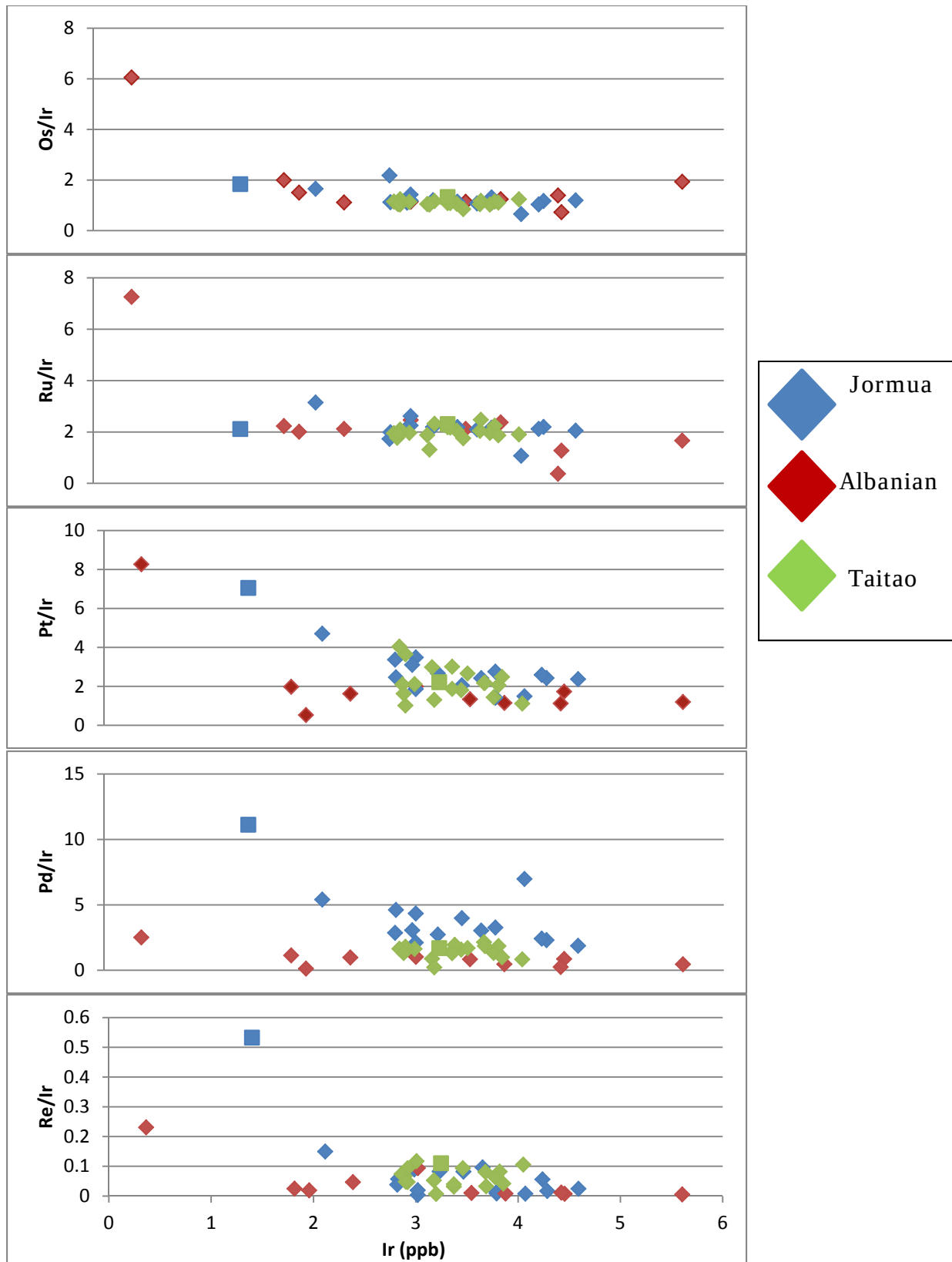


Figure 10 Plot shows the inter-element ratios for Jormua, Albanian and Taitao peridotites. Dunites are indicated by square symbols, other peridotites are symbolized by diamonds.

Inter-element ratios from the Albanian ophiolite were plotted alongside those of the Taitao ophiolite. The compatible HSE/Ir does not change and is close to 1. The inter-element ratios of the Jormua ophiolite do not significantly deviate from those observed in more modern ophiolites (Figure 9).

VI. Discussion

Tectonic Origin of the Albanian Ophiolite

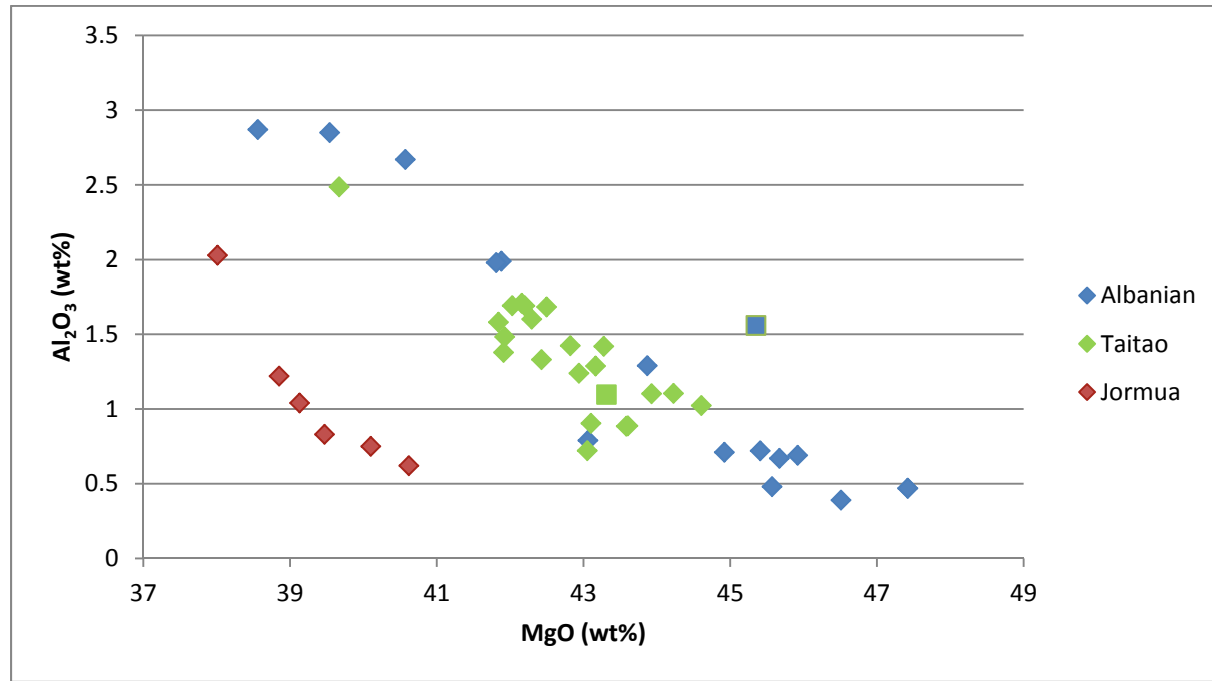


Figure 11 Plot shows the concentration of Al₂O₃ against MgO for the Albanian, Taitao and Jormua ophiolites. Dunites are indicated by square symbols, other peridotites are symbolized by diamonds.

Major element oxides can show the tectonic character of an ophiolite. In MOR type and other subduction unrelated ophiolites, incompatible elements like Al become strongly depleted with increasing compatible element concentrations. Typical major element data for the Antinmaki and Lehmivaara blocks of the Jormua ophiolite is taken from Peltonen et. al, 1998 and is plotted against Os concentration of ATK57-A, ATK76, ATK96 and ATK600 of the Antinmaki block and LHV21 and LHV22 of the Lehmivaara block. The Jormua and Taitao ophiolites are considered MOR-type and demonstrate this trend (Peltonen et. al, 1998; Shibuya et. al, 2007). Samples analyzed from the Albanian ophiolite have a large range of Al₂O₃-MgO concentrations and are also depleted in Al₂O₃. Like those of other MOR ophiolites, most peridotites from the Albanian ophiolite become more depleted in Al₂O₃ as MgO concentration increases (Fig. 10).

However, the Albanian sample A286 is a dunite with SSZ-type character as shown by a relative enrichment of Al₂O₃ (Fig. 10). Overall, it can be asserted that the western chain of the Albanian ophiolite, where most of these samples were extracted from, is predominantly of MOR-type origin.

Osmium Isotopic Composition

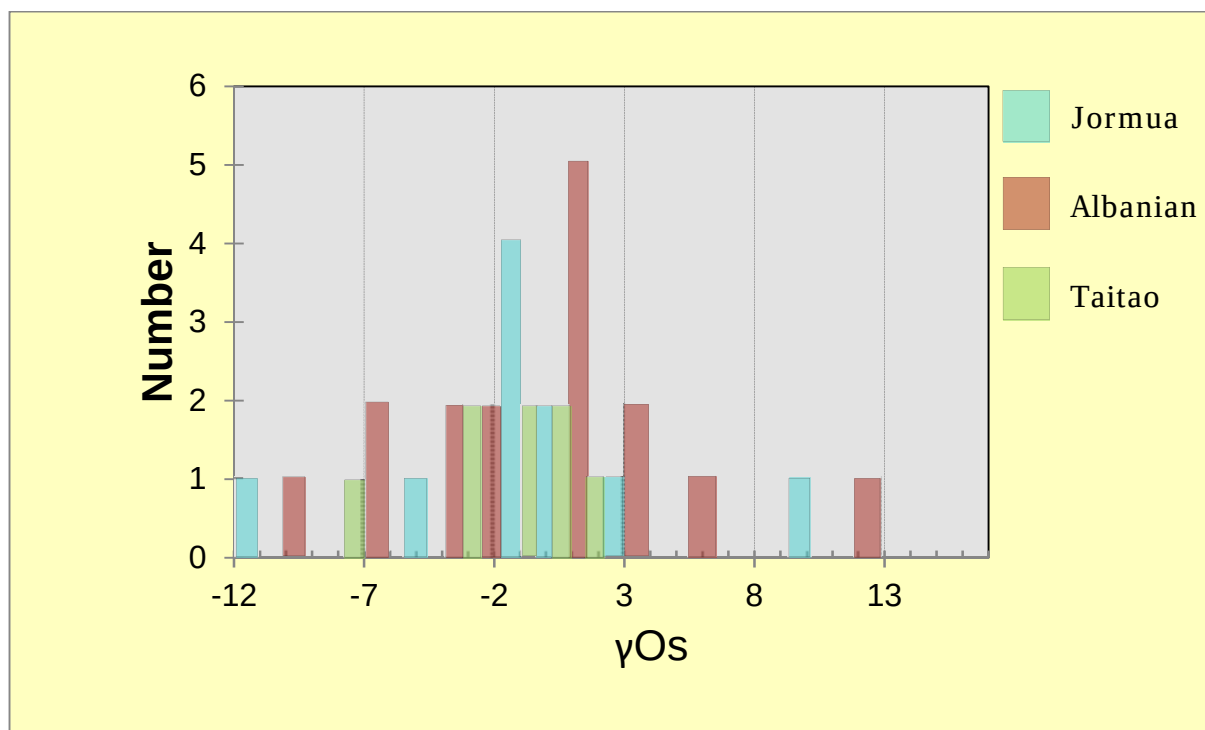


Figure 12 Plot shows the modal distribution plot of γOs in the Jormua, Albanian and Taitao ophiolites.

The Jormua ophiolite's average γOs is -1.32 and ranges from -10.69 to 8.70 in the samples analyzed. The Albanian ophiolite's average γOs is -0.82 and γOs ranges from -9.29 to 10.72 in the samples analyzed. The Taitao ophiolite's average γOs is -2.12 and ranges from -7.99 to 1.98 in the samples analyzed. The average and modal γOs is essentially identical in all three ophiolites. The range of γOs is slightly greater in the Albanian ophiolite than in the Jormua ophiolite. The Taitao ophiolite demonstrates a narrower range of γOs than the other ophiolites (Fig. 11).

Though these data suggest the peridotites of the Albanian ophiolite have a similar average γOs and a greater range of γOs , the difference is not very significant. The average and range of γOs values is greater in the Albanian ophiolite within statistical uncertainty, however the Taitao ophiolite had the lowest average γOs and narrowest range of γOs values of all ophiolites measured.

Highly Siderophile Element Concentration

In terms of HSE concentration, a similar evolution path can be seen. There is a greater variability between incompatible and compatible HSE in the Jormua ophiolite compared to the Albanian ophiolite. This is not a large difference, however (Fig2. 6, 7).

Additionally, the inter-element ratios of all three ophiolites follow a similar pattern for all HSE. With the exception of Jormua samples with low Ir, all samples show similar variability

between incompatible and compatible HSE. The low Ir samples in the Jormua may be dunites, rocks in which incompatible HSE have greater compatibility during mantle melting (O'Driscoll et. al, 2012). However, all samples were reported as serpentinites in Tsuru et. al, 2000. Regardless, the data suggest very little evolution in the concentrations of HSE in the convecting upper mantle.

VI. Conclusion

To study the secular evolution of the convecting upper mantle, I propose to examine the changes in highly siderophile element (HSE) concentration and Os isotopic composition between ophiolites of different ages. There is a difference in compatibility among the HSE, allowing me to analyze their concentrations to determine the extent of chemical depletion and addition processes in the convecting upper mantle. Metasomatic processes add incompatible HSE to mantle rocks.

I hypothesize that Phanerozoic mantle will be enriched in incompatible HSE compared to Proterozoic mantle. Multiple metasomatic events between ancient melt depletion and ophiolite formation will enrich incompatible HSE compared to compatible HSE in the Phanerozoic mantle. I hypothesize that enrichment of incompatible HSE by metasomatism surpassed depletion of incompatible HSE by melting, leading to greater variability among HSE in Phanerozoic mantle.

Osmium isotopic composition can illuminate ancient melting events experienced by an ophiolite. A lower $^{187}\text{Os}/^{188}\text{Os}$ indicates that an ancient melting event removed Re from the system. Over time, the $^{187}\text{Os}/^{188}\text{Os}$ will grow more slowly in a rock from which Re was removed.

The first of my hypotheses, that the Proterozoic mantle would have a lower average γOs has not been supported. The γOs of all three ophiolites are essentially identical.

There is no significant difference in the ranges of γOs in the Albanian ophiolite than the Jormua ophiolite, refuting my second hypothesis.

My final hypothesis, that the variability of HSE concentration would be greater in the Phanerozoic mantle, was not supported by this data. Rather, there seems to be no difference in variability of HSE between Phanerozoic and Proterozoic mantle.

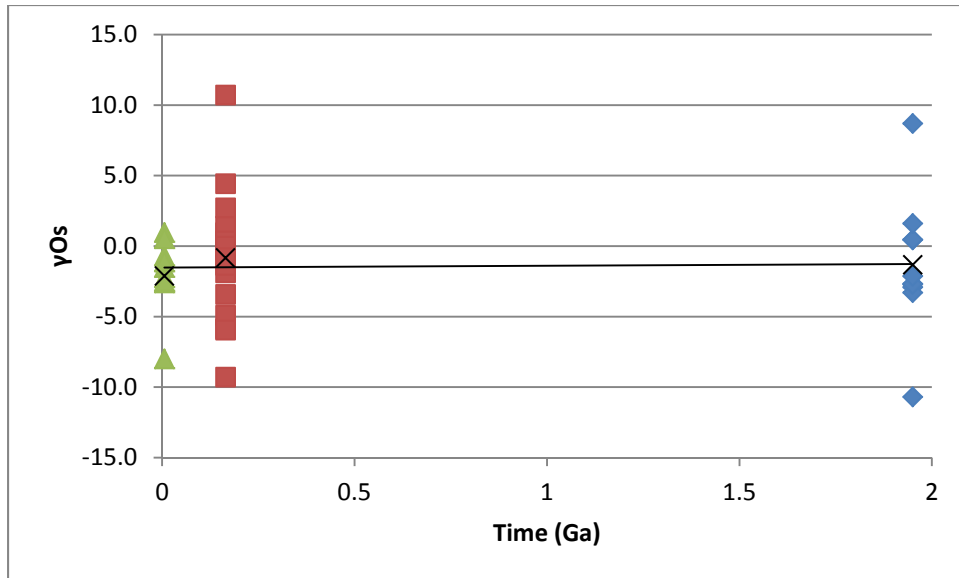


Figure 12 This plot shows the evolution of γ_{Os} in the convecting upper mantle based on this project. Averages of each ophiolite are indicated by crosses. The Os isotopic heterogeneity does not seem to change between 1.95 and 0.006 Ga.

Through the refutation of my hypotheses, the data collected in this project suggest no change in the heterogeneity of Os isotopic composition and HSE concentration in the convecting upper mantle from 1.95 Ga to 0.006 Ga. As time advances, rather than the mantle becoming less chondritic as I predicted, the Os isotopic composition is just slightly less radiogenic than chondritic (Fig. 12). The PUM has been believed to be relatively chondritic in terms of Os isotopic composition in Earth's early history (Meisel et al., 1996). The results of this project show that while heterogeneity can develop, the average deviance of the convecting upper mantle from chondritic $^{187}Os/^{188}Os$ does not change over time. The assumption that the mantle remained relatively chondritic in terms of Os isotopic composition is one of the basic tenets of mantle geochemistry (Tsuru et al. 2000, O'Driscoll et al., 2012). This would be better understood by analyzing MOR-type ophiolites which were obducted at 1 Ga. The average γ_{Os} does not reflect the wide variation of Os isotopic composition seen in all ophiolites, so more work should be done on these sites to better characterize their place within the evolution of the convecting upper mantle.

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