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1

Hard Rock Geochemistry and Earth Mantle Evolution

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1. Introduction

The crust, upper mantle, lower mantle, outer core, and inner core are the textbook subdivisions of the Earth's interior. The core is composed mostly of iron and is so hot that the outer core is molten. In contrast, the inner core is under such extreme pressure that it remains solid. Most of the Earth's mass, is in the mantle and composed of silicates of iron, magnesium, calcium and aluminium. At $> 1000^{\circ}$ C, the mantle is solid but can deform slowly in a plastic manner. The crust is much thinner than any of the other layers, and its mineralogy is dominated by the less dense calcium and sodium aluminium-silicates. Being relatively cold, the crust is brittle, which is the precondition to cause earthquakes.

The physical background of this model is based on recordings of seismic waves from such crustal earthquakes. Seismic waves bend and reflect at the interfaces between different materials. In addition, the two types of seismic wave behave differently, depending on the material. Compressional waves travel and refract through both fluid and solid materials. Shear waves, however, cannot travel through fluids like melts or water.

These geophysical observations had to be explained in a consistent geochemical Earth evolution model. In this challenge petrologists have been mainly restricted to secondary information of the layers. The mantle can only be directly investigated on the base of mantle fragments (xenoliths) that are transported by magma during its rise to the surface. Other approaches are the composition of primary mantle magmas reflecting the mantle source geochemistry. However, the really deep layers, can only be reached in Hollywood science fiction productions, e.g. to save the Earth from catastrophe by a drill down to the core (The Core). Even with the most optimistic news of technical evolution, this remains wishful thinking and a borehole will not be able to reach the core. As a result, analogues had been of primary interest, and observations from astrophysics as well as from meteorites have been able to fill the observational gaps. Iron meteorites are today considered as equivalents to the Earth core. This situation leads modern petrology to consistent model assumptions and such a model will be discussed in this



paper. In the next section an approach for the mantle composition and evolution will be discussed, on the base of primary mantle magmas.

2. Volcanoes and primary mantle melts

A volcano is an opening in the Earth's surface that allows hot, molten rock, and gases to escape from deep below the surface. The word 'volcano' comes from the little island Vulcano (38°24'00"N, 14°58'00"E) in the Tyrrhenian Sea, about 25 km north of Sicily and the southernmost of the Aeolian Islands. Centuries ago, people believed that Vulcano was the chimney of the forge of Vulcan - the blacksmith of the Roman gods. Volcan was named in the Greek mythology Hephaistos - the god of fire and craftsmanship. Romans thought that the hot lava fragments and clouds of dust erupting form Vulcano came from Vulcan's forge as he hammered thunderbolts for Jupiter, king of the gods, and weapons for Mars, the god of war. Today geoscientists attribute the volcanic activities at Vulcano and other volcanoes mainly to release of excess heat by geodynamic plate tectonic processes. The plate tectonic theory was developed to explain the observed evidence for large scale motions of the Earth's crust.

Next to the division of the Earth in crust, mantle and core, geodynamists use another classification of the crust and the mantle. This division of the outer parts of the Earth into lithosphere and asthenosphere is based on their mechanical properties. The lithosphere is cooler and more rigid, whilst the asthenosphere is hotter and mechanically weaker. Also, the lithosphere loses heat by conduction whereas asthenosphere transfers heat by convection and has a nearly adiabatic temperature gradient. The lithosphere comprises both crust and upper parts of the mantle. The key principle of plate tectonics is that the lithosphere exists as separate and distinct tectonic plates, riding on the visco-elastic solid asthenosphere. The plate boundaries are commonly associated with geological events such as earthquakes and the creation of mountains, volcanoes and oceanic trenches. The majority of the world's active volcanoes occur along such plate boundaries, with the Ring of Fire around the Pacific being the most active and famous.

Plates are able to move because of the relative density of oceanic lithosphere and the relative weakness of the asthenosphere. Dissipation of heat from the mantle is recognized to be the original source of energy driving plate tectonics, but it is no longer thought that the plates ride passively on asthenospheric convection currents. Instead, it is accepted that the excess density of the oceanic lithosphere sinking in subduction zones drives plate motions. When it forms at mid-ocean ridges (MOR), the young hot oceanic lithosphere is initially less dense than the underlying asthenosphere, but it becomes more dense with age, as it conductively cools. The greater density of old lithosphere relative to the underlying asthenosphere allows it to sink into the deep mantle at subduction zones, providing most of the driving force for plate motions.

Three types of plate boundaries are distinguished by the way the plates move relative to each other.

- 1. Transform boundaries (where two plates slide against each other);
- 2. Convergent boundaries (where two plates collide head-on with each other); and
- 3. Divergent boundaries (where two plates move apart from each other).

Fig. 1: (A) Photograph of an ODP (Leg104 642E) MORB core sample from the N Atlantic, and (B) Cross polarized light microphotograph of a typical tholeiitic MORB from the N Atlantic (C) Photo of the unique IODP scientific research vessel Joides Resolution, specially designed to drill deep into the sea floor (Photo C from www-odp.tamu.edu).

Transform boundaries have only limited magmatic activity and due to this observation they can not be used for the geochemical evolution of the mantle. In contrast both other boundary types are strongly associated with enormously igneous activity.

A convergent plate boundary forms at a subduction zone when one or both of the tectonic plates is composed of oceanic lithosphere. The less dense plate, or lithosphere usually rides over the denser plate, which is subducted. This type of plate convergence is associated with (volcanic) island arcs such as e.g. Japan or, the Andes. In subduction zones, the loss of volatiles from the subducted slab into the mantle induces partial melting of the overriding metasomatized mantle and generates low-density, calc-alkaline magma that buoyantly rise through the lithosphere of the overriding plate. As a result the extruded magmas are the product of a combination of volatiles from the subducted slab and mantle material. Hence, the erupted magmas will not have a primary primitive mantle signature. The divergent boundaries within continents initially produce rift valleys (e.g. the Rhinegraben). Not all continental rifts eventually evolve to the stage of continental breakup. The so-called "failed" rifts were once loci of strain localization and crustal extension, but are now no longer considered active. Other rifts proceed more successfully to their final stage and result in continental separation and seafloor spreading with oceanic crust formation. Therefore, most active divergent plate boundaries exist between oceanic plates and are called mid-oceanic ridges (MOR). At MOR crystallized magma (MOR basalts, MORB) (Fig. 1a, 1b) continuously forms new oceanic crust along the ridge axes. This new magma emerges at and near the axis because of decompression melting in the underlying Earth's mantle. Due to this constant fusion process, with homogeneous tholeiitic magmas (named after the rock Tholeyit of Tholey, Saarland), these rocks have



the highest geochemical potential to start a geochemical investigation of the mantle evolution. During the last years MORB have been thoroughly petrologically investigated during the different international ocean drilling programs (Fig. 1).

3. The chemistry of the solar system and the cosmic composition

The early geochemical evolution of material from the Earth has to be seen in the context of cosmochemistry, as the Earth is only a part of our solar system. Geologically it is the most studied planet. However, the chemistry of meteorites are crucial for understanding and modelling the bulk Earth composition. A fundamental constrain on any understanding of the chemical evolution of the Earth is the abundance of elements in the solar system. Due to the fact, that the planets are generally thought to have originated in a slowly rotating disk-shaped "solar nebula" of gas and dust with solar composition.

Some meteorites, the Chondrites, are chemically primitive, having com-

Fig. 3: REE pattern illustrating the Earth differentiation into core, mantle and crust. The REE concentration had been more than 3 times enriched in the primitive mantle compared to the cosmic composition after the separation of the Earth into core and mantle. This primitive mantle has been depleted in the light REE during the formation of the crust, the resulting depleted mantle is today the source of the N-MORB. In contrast the opposite reservoir, the continental crust is enriched in light REE compared to the primitive mantle. The average N-MORB composition and the average continental crust content, as well as the normalizing C1 Chondrite data are from the GERM Reservoir Database (http://Earthref.org).

positions similar to that of the sun. Chondrites are named after the rounded fragments, a.k.a. chondrules that they contain. The C1 or CI Chondrites have the most primordial composition and features and are used to supplement solar values in the estimation of cosmic composition (Fig. 2).

4. Geochemical information on mantle evolution

The MORB geochemistry is a key to understand the geochemical evolution of the Earth. The major element MORB chemistry is relatively homogeneous, so that nearly every oceanic crustal segment around the world has a very similar composition. Trace elements like the lanthanides, or rare earth elements (REE), have important applications in igneous and metamorphic petrology. The REE comprise the series of elements with atomic numbers 57 to 71 (La to Lu). The REE are the upper line of the two rows of elements commonly shown at the bottom of the periodic table. The REE all have very similar chemical and

Fig. 2: Schematic sketch of the chemical differentiation of the Earth from a homogeneous cosmic composition into core, mantle and crust.

physical properties. This is based on the fact, that they all form stable 3+ ions of similar size. The only differences in chemical behaviour are a consequence of the small but steady decrease in ionic size with increasing atomic number. A small number of the REE also exist in oxidation states other than 3+ but the only geological important ions are Ce4+ and Eu2+. These form a smaller and a larger ion relative to the common 3+ oxidation state. Because of their high charge and large radii, the REE are incompatible elements. Incompatible elements are in geochemistry elements that during melting process will be strongly enriched in the melt compared to the solid residues. The crystals are not able to retain these elements during partial melting processes. However, the heavy REE have sufficiently small radii that they can be accommodated to some degree in many common minerals. The heaviest REE readily substitute in garnet, and hence can be concentrated by it. Eu, in its 2+ state, substitutes for Ca2+ in plagioclase feldspar more readily than the other REE. Thus plagioclase is often anomalously rich in Eu compared to the other REE, and other phases in equilibrium with plagioclase become relatively depleted in Eu as a consequence. REE patterns for average mid-ocean ridge basalt (N-MORB) are shown in Figure 3. MORB exhibits a light





Fig. 4: ¹⁴³Nd/¹⁴⁴Nd vs. ⁸⁷Sr/⁸⁶Sr diagram for igneous rocks from the North Atlantic Igneous Province (NAIP) LIP. Isotopic differences are due to the contrast in Nd and Sr isotopic composition between old continental crust (e.g. gneiss, amphibolites) and mantle magma sources. Variations of ¹⁴³Nd/¹⁴⁴ Nd and ⁸⁷Sr/⁸⁶Sr in crustal rocks are related to age and the contrasting geochemical behaviour of Sm and Nd relative to Rb and Sr. The mantle plume model suggests that the correlation of initial Nd and Sr isotopes represent mixing lines, between "mantle zoo" reservoirs of distinct chemistry and age. DMM = Depleted MORB Mantle; DMM = Depleted MORB Mantle; HIMU = High μ (subducted oceanic crust); EM1 and EM2 = Enriched Mantle 1 (recycled pelagic ocean floor sediments / sub-continental lithosphere) and 2 (subducted continental material). Alternatively, the trend may result from mixing by assimilation / contamination of high-Sm/Nd, low-Rb/Sr mantle melts with old low-Sm/Nd, high-Rb/Sr crustal material, as has been shown in some sub-NAIP areas (Scotland). (Figure from Meyer et al., in press)

REE depleted pattern reflecting the incompatible element-depleted nature of the upper mantle from which these magmas are derived. This incompatible element depletion of the mantle is generally thought to have resulted from extraction of partial melts, in which the incompatible elements were concentrated. In a theoretical model where the continental crust and the mantle are the only two REE reservoirs, and decompression melts from the upper mantle are light REE depleted, then the continental crust complementary reservoir has to be light REE enriched (Fig. 2). This model is supported by data in Figure 3: the upper continental crust has a light REE enriched pattern with a so-called negative 'Eu anomaly'. The available geochemical dataset allows to conclude, that the complementary incompatible-element enriched reservoir is the continental crust.

The most prominent igneous rocks on the Earth surface – the MORB – have a common mantle source, the geochemically depleted upper mantle (DM) (Fig. 2). It can be concluded that during extensional processes resulting in MOR this depleted reservoir is the major fused mantle involved in this geodynamic process.

Most of the magmatic activity on Earth is limited to the plate boundaries, however magmatism in the middle of plates is also known (e.g. Eifel, Hawaii). After the introduction of the mantle plume hypothesis (Morgan, 1971) this so-called intraplate volcanism has mainly been explained by hot spots. In the mantle plume hypothesis geochemically enriched material from subducted slabs is stored for geological times at the D" (core - mantle boundary). During this period the enriched material equilibrates with the surrounding pressure/temperature conditions, and starts to rise again due to its smaller density compared to the lower mantle. Such a rising plume is restricted to a relatively small area on the surface, and is believed to be a nearly fixed system compared to the plate movements. The rising mantle plume material starts to melt due to its excess temperature at the asthenosphere - lithosphere boundary. The arrival of mantle plumes is often related to the formation of Large Igneous Provinces (LIP). The formation of such LIPs has been recently discussed as potential source for biological mass extinctions through the geological history.

During the rise through the mantle, plume material has multiple possibilities for deep mantle interactions. Even geochemical core signatures are believed to be identified in proposed mantle plume derived magmas. Mainly



Fig. 5: Pb isotope ratios in major terrestrial mantle reservoirs MORB and oceanic islands represent the isotopic variability of upper mantle and deep mantle respectively. As an example for intracontinental magmatism are plotted data from the CEVP, the Rhoen Mts. in Germany. (Modified after Meyer et al., 20002).

isotopic investigations (cf. Fig. 4) defined different geochemical reservoirs in the mantle. Isotopes do not fractionate during partial melting of fractional melting processes, so they will reflect the characteristics of the source.

The detected geochemical mantle zoo reservoirs (cf. Fig. 4, 5) are e.g.:

- (1) DM depleted mantle (MORB source),
- (2) BSE Bulk Silicate Earth
- (3) PREMA prevalent mantle
- (4) HIMU (read: high μ=high ²³⁸U/²⁰⁴Pb (Fig. 5)) former subducted and recycled oceanic crust
- (5) EM1 enriched mantle type 1 (has near primordial ⁸⁷Sr/₈₆Sr (Fig. 4)) former subducted and recycled oceanic crust plus sediments
- (6) EM2 enriched mantle type 2 (has > 0.720, well above any reasonable mantle sources high ⁸⁷Sr/
 ⁸⁶Sr (Fig. 4)) former subducted and recycled oceanic crust with sediments

This mantle plume model was for more than 25 years the ultimate explanation for intracontinental magmatism. However, this hypothesis has recently been challenged due to the fact, that several primary classical plume features required adaptations (cf. www.mantleplumes.org). Predictions of the mantle plume hypothesis that are not observed for the Eifel plume are for example, the plume track is nonexistent, and the seismic tomographic image of the mantle anomaly (proposed mantle plume) is restricted to the upper mantle. As for several plumes the mantle anomaly has been observed extending into the deep mantle (Montelli et al., 2004), the lack of continuity below the Eifel seems to be real. Furthermore, the Eifel is an integral area of the Central European Volcanic Province (CEVP), and the CEVP has more signatures to be rift, instead of mantle plume, related.

Moreover, several isotopically enriched reservoirs (EMI, EMII, and HIMU) (Fig 4) are too enriched for any known mantle process, and they correspond to crustal rocks and/or sediments. In the plume concept this reservoirs had been produced in the mantle through subduction of oceanic crust with different (continental) crustal segments. This package has been recycled in the deeper mantle. However, these enriched signatures can also be produced by mantle melt / continental crust interactions (EM1 can be an assimilation signature of lower continental crust, and EM2 correlates with a contamination of upper continental crustal rocks). Alternative models for intracontinental magmatic activities have been suggested, including delamination, meteorite impact, small-scale rift-related convection, and chemical mantle heterogeneities.

5. Conclusions

Hard rock geochemistry of igneous rocks provides clear evidence for the chemical evolution of the Earth. The differentiation of the Earth into core, mantle and crust left behind geochemical "fingerprints" (Fig. 2). These signatures can be traced back today in trace element and isotopic characteristics of primary mantle melts. The geochemistry community has good reasons to assume, that the average solar nebula composition is represented by the C1 Chondrite meteorites. Every process of the Earth evolution fractionated this composition. Geochemically the core formation is reflected in the enrichment of the incompatible elements and the depletion of "siderophile" elements (e.g. Au, Ir, Os) in every primary mantle melt source. The light REE depletion of the MORB source can only be explained as the conjugate reservoir of the enriched continental crust (Fig. 3).

Magmatic activity mainly takes place at divergent and convergent plate margins. Volcanism in the middle of plates is less voluminous and the cause of it is more enigmatic. This intraplate activity is today a matter of sharp debate. No obvious mechanism fits readily into the plate tectonic paradigm. Following Morgan (1971) this activity is commonly related to hot spots, deep astenospheric mantle upwellings. However, this scenario is presently strongly debated and alternative models including delamination, meteorite impact, small-scale rift-related convection, and chemical mantle heterogeneities have been proposed. Ongoing development of the different models and availability of increasingly more consistent geochemical data from projects investigating the role of mantle-crust interaction (e.g. ESF EUROMARGINS project CRP-01-LEC-EMA13F) should help to resolve the problem of the challenged mantle plume concept in the near future.

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