

# Sm-Nd and Lu-Hf Isotope Geochemistry of the Himalayan High- and Ultrahigh-Pressure Eclogites, Kaghan Valley, Pakistan

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## 1. Introduction

Eclogites are generally considered as derived from basaltic or gabbroic rocks which have either been intensely metamorphosed during subduction-obduction related processes or, associated with continental crust and affected by major crustal thrusting. The advantage of petrological, geochemical, and geochronological study of eclogitic rocks is twofold. First, metabasic rocks are capable of preserving the original magmatic characteristics of igneous formations. Second, the study of eclogites enables us to appreciate the behaviour of isotopic tracers during high-grade metamorphism.

In this chapter we report Sm-Nd and Lu-Hf isotope compositions of whole rock and their constituent minerals (garnet, clinopyroxene, phengite, and epidote) from the Himalayan high-pressure (HP) and ultrahigh-pressure (UHP) eclogites which are exposed in the Kaghan Valley of Pakistan (Fig. 1). These eclogites were formed when the Indian Plate slab subducted beneath the Asian Plate to greater depths and experienced UHP metamorphism. The Kaghan Valley eclogites have been discussed previously by several authors (e.g. Greco et al., 1989; Pognante & Spencer, 1991; Tonarini et al., 1993; Spencer et al., 1995; Lombardo & Rolfo, 2000; O'Brien et al., 2001; Kaneko et al., 2003; Parrish et al., 2006; Rehman et al., 2008). Spencer et al. (1995) carried out geochemical work (major and trace elements and Sr isotope) on the Kaghan Valley whole rock eclogites. They interpreted based on their geochemical results that the protolith for these eclogites was the Permian Panjal Trap basalts. Similarly, Tonarini et al. (1993) reported an Sm-Nd isochron age of 49 and a Sm-Nd isochron age of  $49 \pm 6$  Ma representing the eclogite facies event in the Himalayan region. They calculated the above age from a garnet-clinopyroxene pair. Spencer & Gebauer (1996) reported a U-Pb zircon SHRIMP age of 44 Ma for the eclogite facies event. In addition, Kaneko et al. (2003)

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reported 46 Ma as the peak time for the UHP event in the Himalayan region. Their result was based on the U-Pb age dating on the coesite-bearing zircon from felsic gneisses which surround the UHP eclogites in Kaghan Valley. Parrish et al. (2006) also reported similar age results deduced from the U-Pb zircon age dating. Recently, Wilke et al. (2010a) elaborated the multi-stage history of the Kaghan Valley eclogites based on the major and trace element geochemistry of the eclogites, and a U-Pb zircon and rutile geochronology from the felsic gneisses. Most of the above mentioned researchers and references therein elaborate the metamorphic history of the eclogites and surrounding felsic gneisses. However, (i) details on the protolith environment of these eclogites, (ii) fluids infiltration effects on these rocks during their subduction to mantle depths, and (iii) element mobility during eclogite facies and late-stage metamorphism remained unclear. To discuss the above problems we reinvestigated the Kaghan Valley eclogites by examining carefully petrological and textural features, and extending our work to multi-isotope (Sm-Nd and Lu-Hf) systematic. Our results enabled us to (i) differentiate between the types of eclogites, (ii) evaluate their source rock, and (iii) effect of fluid infiltration on these eclogites during subduction and later stages of exhumation. Our results provide significant evidence of isotopic disequilibrium during and after the eclogite facies metamorphism.

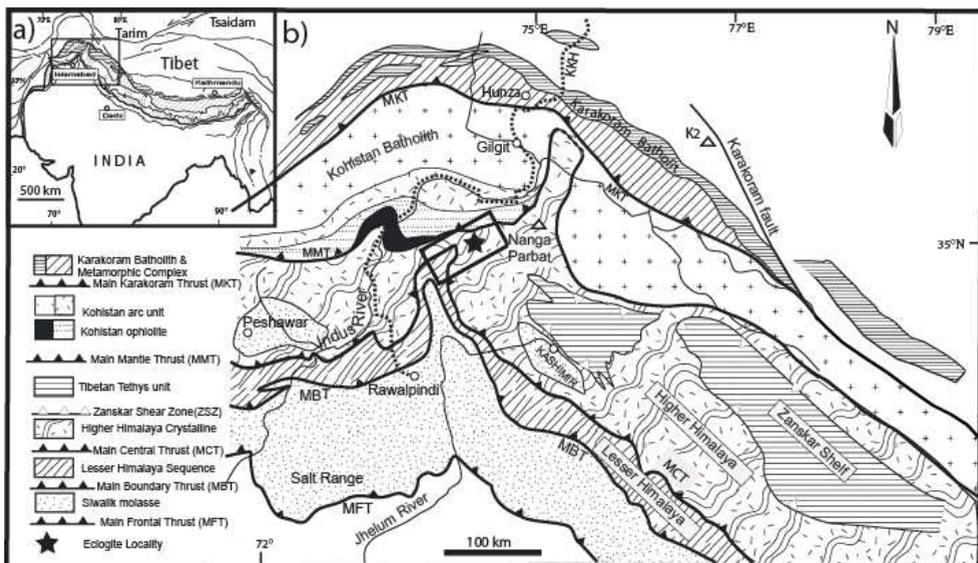


Fig. 1. (a) Geographical location of the Himalayan range. (b) An enlarged portion of the boxed area shown in the upper left, representing main tectonic units of the Indian Plate, the Kohistan arc, and the southern margin of the Asian Plate. Black star and a rectangle surrounding it represent location of the eclogites in the Kaghan Valley transect (see Fig. 2 for details).

## 2. Geological background

Eclogites of the Himalayan chain are the products of continental basaltic flows and their preceding feeder dikes of Permian to Lower Triassic Panjal Trap (e.g. Honegger et al., 1982;

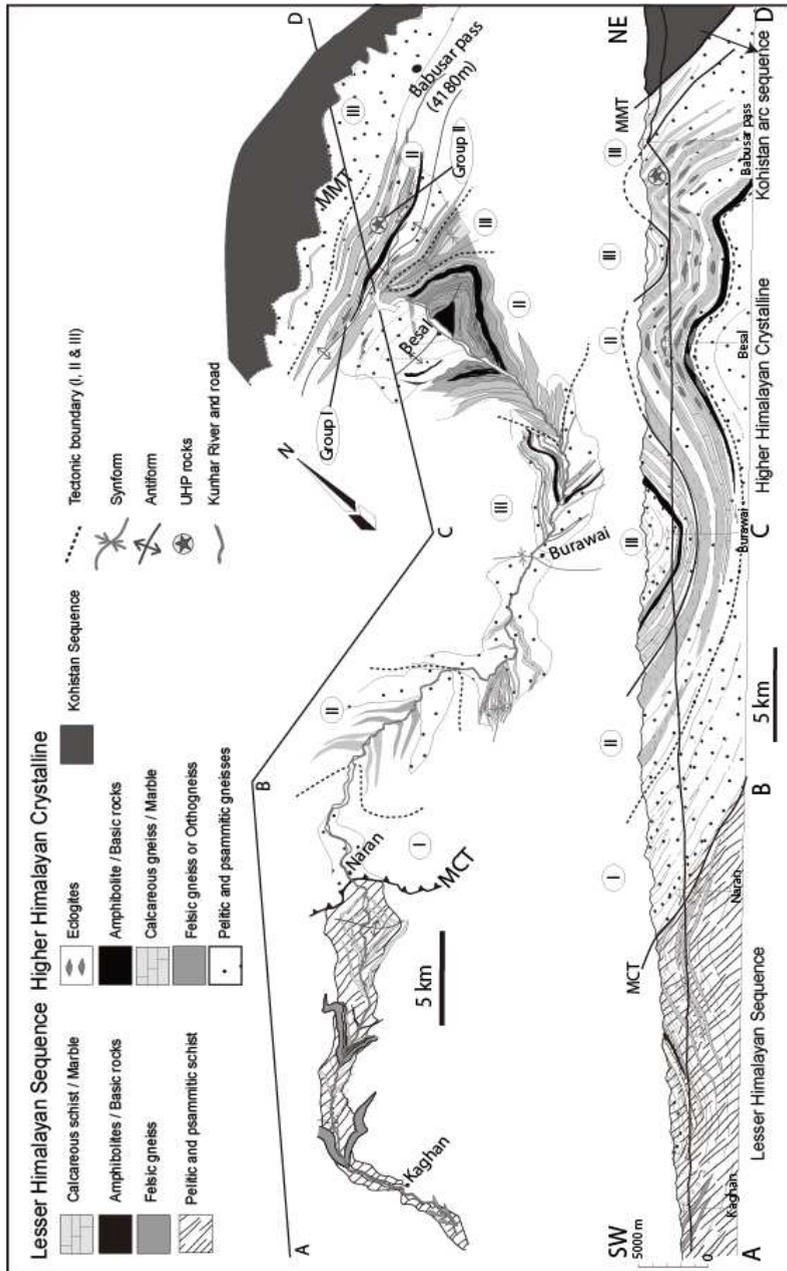


Fig. 2. A geological map with cross-section of the Himalayan metamorphic belt along the Kaghan Valley transect. Abbreviations used in map are; MCT: Main Central Thrust; MMT: Main Mantle Thrust (for further details on the rock types and structures, see Rehman et al., 2007, 2008). The map is modified after Kaneko et al. (2003).

Spencer et al., 1995). These basaltic extrusions at the northern margin of the Indian Plate mark start of the Himalayan cycle (Honegger et al., 1982). During the Himalayan cycle the volcanic activity began in the Upper Carboniferous, with the climax in Lower Permian, producing several hundred meters of intermediate to acid pyroclastic and welded tuffs overlying Carboniferous shales and shallow water limestone (Honegger et al., 1982). The onset of India-Asia collision ranging from 65 Ma to 40 Ma resulted in deep subduction of the Indian Plate beneath the Asian Plate (e.g. Patriat & Achache, 1984; Beck et al., 1995; Guillot et al., 2003). This subduction and related metamorphism resulted in a large-scale thrusting and piling up of the oceanic crust and sediments in the form of the Lesser Himalayan sequence, the Higher Himalayan crystalline and the Tethyan sediments as well as the ophiolitic mélanges along the suture zone between the Indian Plate and the Kohistan island arc (Greco et al., 1989; Spencer et al., 1995; Rehman et al., 2007) (Fig. 2).

In the Kaghan Valley transect a geological section is exposed which comprises the Lesser Himalayan sequence, the Higher Himalayan Crystalline, and the basement rocks of the Kohistan island arc (Fig. 2). Information on petrological, geochemical, and structural geology of the above sequences are explained in detail elsewhere (e.g. Rehman et al., 2007; 2008 and references therein). In this session, we will explain mafic rocks mainly. The mafic sheets exposed in the Higher Himalayan Crystalline in the Kaghan Valley, range in size from a few meters to few tens of meters within pelitic gneisses and marbles. Greenschist and amphibolite facies overprint on earlier eclogite facies assemblages. Coesite-bearing UHP eclogite is found as an isolated block (for locations see Rehman et al., 2007, 2008). The presence of coesite pseudomorphs in omphacite in eclogites, and in zircon from gneisses (Kaneko et al., 2003) indicate that these rocks reached a depth exceeding 100 km when the leading edge of the Indian Plate subducted beneath the Asian Plate.

### 3. Field occurrence and petrography of eclogites

Eclogites in the Kaghan Valley occur as massive and extend for a few tens of meters (Fig 3a, b) and as an isolated boudines or lenses 2 to 3 m in diameter (Fig. 3c, d). They are hosted by felsic gneisses, marbles and amphibolite sheets. These eclogites were subdivided into Group I and II (Fig. 4). Both groups of eclogites are differentiated from each other on the basis of occurrence, mineralogy, and geochemistry. Group I eclogites are composed of garnet, clinopyroxene, quartz, amphibole with rare epidote and phengite. They contain rutile, ilmenite, apatite, and abundant zircons as accessory minerals. Group II eclogites are composed of garnet, clinopyroxene, quartz/coesite, phengite, epidote, and amphibole with accessory rutile, ilmenite, apatite, and rare zircon.

Group I eclogites are HP and record pressure-temperature conditions at  $704 \pm 92$  °C and  $2.2 \pm 0.3$  GPa, whereas, Group II eclogites are UHP and recorded pressure-temperature conditions between 2.7 and 3.2 GPa and 757 and 786 °C respectively (Rehman et al., 2007).

Based on petrographic features and mineral inclusion study three apparent stages of metamorphism have been reported in the Himalayan eclogites of Kaghan Valley (Rehman et al., 2008). The first stage represented a prograde garnet growth stage (jadeite + quartz + albite inclusions in garnet core). The second stage represented peak UHP stage (deduced from the presence of coesite inclusion in clinopyroxene and pressure-temperature conditions estimated from the chemical composition of the rim portions of adjacent garnet, clinopyroxene and phengite). The third stage was a decompression/retrogressive stage

represented by the common occurrence of symplectitic augite, amphibole, and quartz after clinopyroxene. The third stage recorded texturally late-stage amphibolite facies overprint. Reaction textures and phase relations indicate that the metamorphic overprint was largely under hydrous conditions.

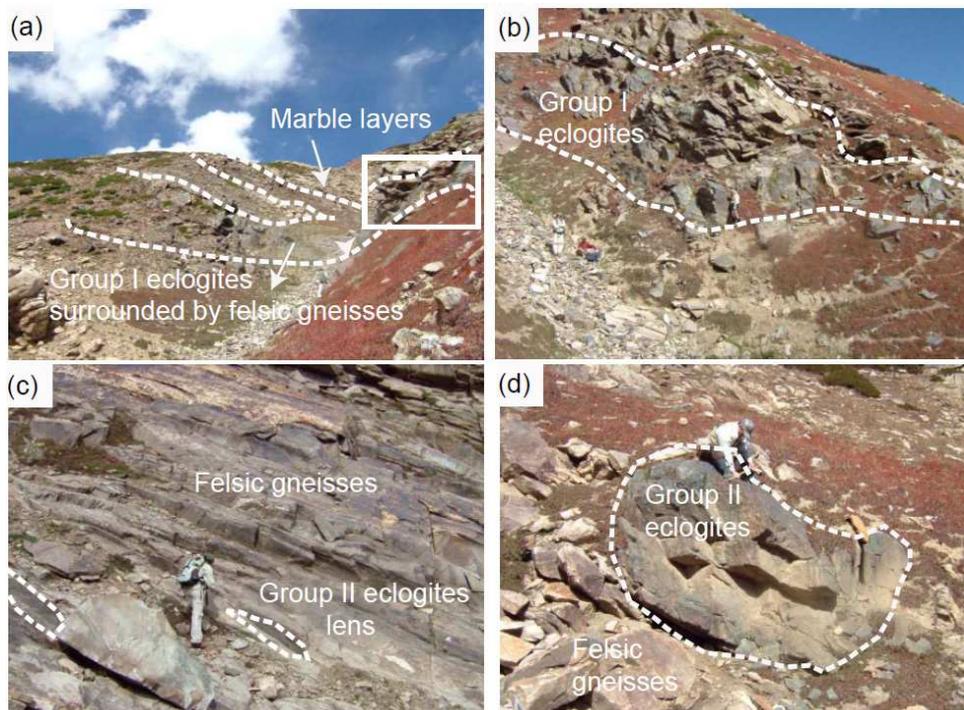


Fig. 3. Field photographs of eclogite types exposed in the Kaghan Valley. (a) Group I (massive) eclogite exposed in the northwest of Lulusar lake (for location see Fig. 4). (b) Closer view of the boxed area shown in the upper right in photograph on the left. (c) Group II (lens type) eclogite exposed in the northwest of Giti das (for location see Fig. 4). (d) Group II (boudine) eclogite exposed in the same gorge located northwest of Giti das (for location see Fig. 4).

#### 4. Analytical methods

Geochemical analytical procedures were performed at the Pheasant Memorial Laboratory (PML), Institute for the Study of the Earth's Interior (ISEI), Okayama University at Misasa, Japan, following the procedures of Nakamura et al. (2003), Lu et al. (2007), and Makishima & Nakamura (2007). Basaltic standard (JB3) from the Geological Survey of Japan was used as a standard. Five eclogite samples (whole rock powders of two samples from the Group I and three samples from the Group II eclogites) and 15 mineral separates of the same five eclogite samples from both groups were decomposed and analyzed for their Sm-Nd and Lu-Hf isotopic ratios and abundances. Garnet and clinopyroxene separates from Group I and II eclogites and epidote and phengite from Group II eclogites were handpicked (Group I

did not contain phengite and epidote). To remove surface contamination, garnet and clinopyroxene were washed using ultrasonic bath, with 6 M HCl till the yellow color faded away, whereas epidote and phengite were washed with 2 M HCl for 30–40 minutes, and rinsed with distilled water few times. Then distilled water was added to all mineral separates and put for washing in an ultrasonic bath for overnight for complete removal of any contamination. After drying, the separated mineral fractions were further pulverized using agate mill and mortar. The powdered fractions were further leached with 0.1 N HCl till the yellow color faded away. Then rinsed with distilled water few times to remove any remaining contamination and dried at 70 °C. Powdered samples were decomposed in Teflon Bombs added with concentrated HF and HClO<sub>4</sub> at 245 °C for 4 days to get complete digestions. The solutions were then transferred to Teflon beakers, added with 0.1, 0.6 and 0.3 ml of HF, HClO<sub>4</sub> and HNO<sub>3</sub> respectively and put for agitation in ultrasonic bath for 8 hours to get complete homogenous solution. Fluoride residues produced by the initial acid attack were removed by repeated redissolution in HClO<sub>4</sub> following the procedures of Yokoyama et al. (1999).

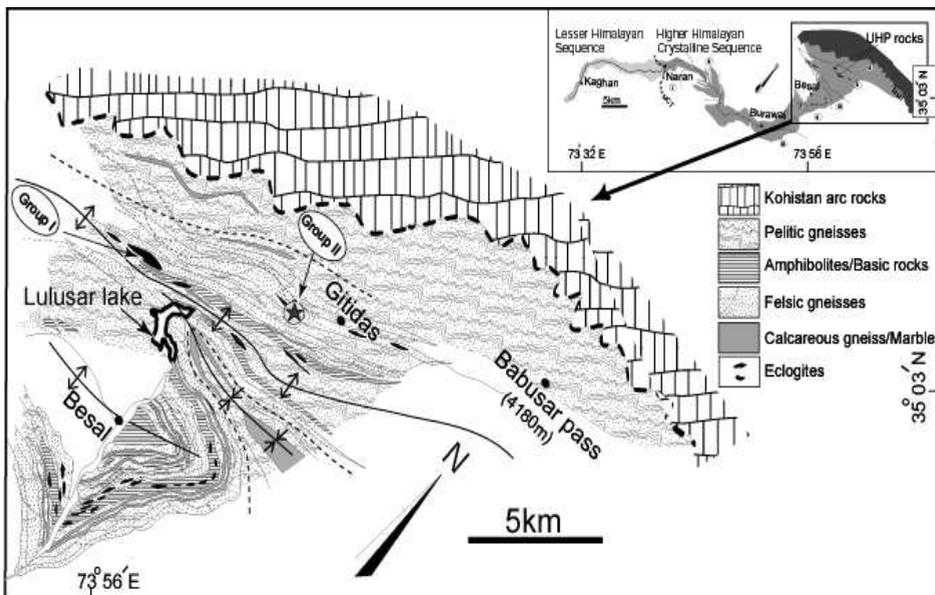


Fig. 4. Location of the Group I and II eclogites. The location map is zoomed area of the box shown on the upper right, which is a reduced/modified form of the geological transect map shown in Fig. 2 (modified from Kaneko et al., 2003; Rehman et al., 2007).

The analytical procedures for mass spectrometry following Yoshikawa & Nakamura (1993) for Nd isotopic ratios and abundances of Sm and Nd, employing Thermal Ionization Mass Spectrometer (TIMS: Finnigan MAT262) in static multi-collection mode. To determine the isotopic ratios and abundances of Sm and Nd, a fraction of decomposed sample solution was successively separated from each of the whole rock and separated minerals, using a multi-ion exchange column chemistry approach modified after Nakamura et al. (2003). In each sequence JB3 standard was decomposed which yields typical analytical reproducibility

of less than 0.005% Nd isotopic ratio, respectively, and < 1% for Sm and Nd abundances. Chemical separation procedures for Lu-Hf follow after Lu et al. (2007) using multi-ion exchange column chemistry. Lutetium was successively separated from the same solution as those used for Sm and Nd. Hf isotopic ratios, and Hf and Lu abundances were determined using multi-sector ICP-MS (Neptune) at the PML following the method of Makishima & Nakamura (2007). Accuracies of the isotopic ratio and element concentrations were confirmed by repeated measurement of JB3 standard solutions. Isotopic fractionation during analysis was corrected using  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  as normalizing factors. Instrumental mass discrimination of TIMS analyses was corrected by the  $^{143}\text{Nd}/^{143}\text{Nd}$  (La Jolla) values of standards ( $0.511874 \pm 0.000020$ ,  $n=10$ ). The Hf isotope ratios were normalized to JMC 475=0.282160. Total procedural blanks for digestion and column chemistry were < 12, < 2, < 2, and < 10 pg for Lu, Hf, Sm and Nd respectively; sample sizes were sufficiently large so that blanks were negligible and blank corrections were unnecessary, however, for Sm and Nd we used blank corrected values.

Values used for age calculations and initial isotope compositions are based on the decay constants  $\lambda^{176}\text{Lu} = 1.865 \times 10^{-11} \text{ year}^{-1}$  (Scherer et al., 2001) and  $\lambda^{147}\text{Sm} = 6.54 \times 10^{-12} \text{ year}^{-1}$  (Lugmair & Marti, 1978 and references therein). The chondritic uniform reservoir (CHUR) parameters used for calculating initial  $\epsilon\text{Hf}$  and  $\epsilon\text{Nd}$  values are  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282818$  (White, 2011),  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0334$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$  recalculated using  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  to correct for mass fractionation, and  $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$  (Faure, 1986). Age calculations (Sm-Nd and Lu-Hf isochrones) were made using Isoplot 3.6 (Ludwig, 2009).

## 5. Results

Major and trace element compositions of the Himalayan Group I and II eclogites in the Kaghan Valley have been reported elsewhere (Rehman et al., 2008) in which all the eclogitic samples have basaltic compositions with 42 ~ 50 wt. %  $\text{SiO}_2$ , and display tholeiitic differentiation trends. Group I eclogites are FeO-TiO<sub>2</sub> rich (FeO: 15 to 18 wt. %, and TiO<sub>2</sub>: 2 to 5 wt. %), whereas Group II eclogites are comparatively less enriched in FeO and TiO<sub>2</sub>. Present paper focuses on the Sm-Nd and Lu-Hf isotope compositions and in the following sections we will describe the isotopic results only.

### 5.1 Sm-Nd isotope geochemistry

The Sm-Nd isotopic compositions of five whole rock eclogite samples (2 samples from Group I and 3 samples from Group II eclogites) were determined (Table 1). In addition, we also determined the Sm-Nd compositions of 15 mineral separates (garnet, clinopyroxene, epidote and phengite) from the above mentioned five whole rock eclogites.

#### 5.1.1 Group I eclogites

Sm and Nd contents,  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios for the whole rock eclogites (Sample Ph380 and Ph381) and for garnet and clinopyroxene from the above two samples have been analysed. Results are plotted in Fig. 5 and are shown in Table 1.

In sample Ph380 the Nd contents are 4.69 ppm in garnet, 10.99 ppm in 41 clinopyroxene and 39.77 ppm in whole rock. Similarly the Sm contents are 3.93 ppm in garnet, 3.48 ppm in clinopyroxene and 10.85 ppm in whole rock.

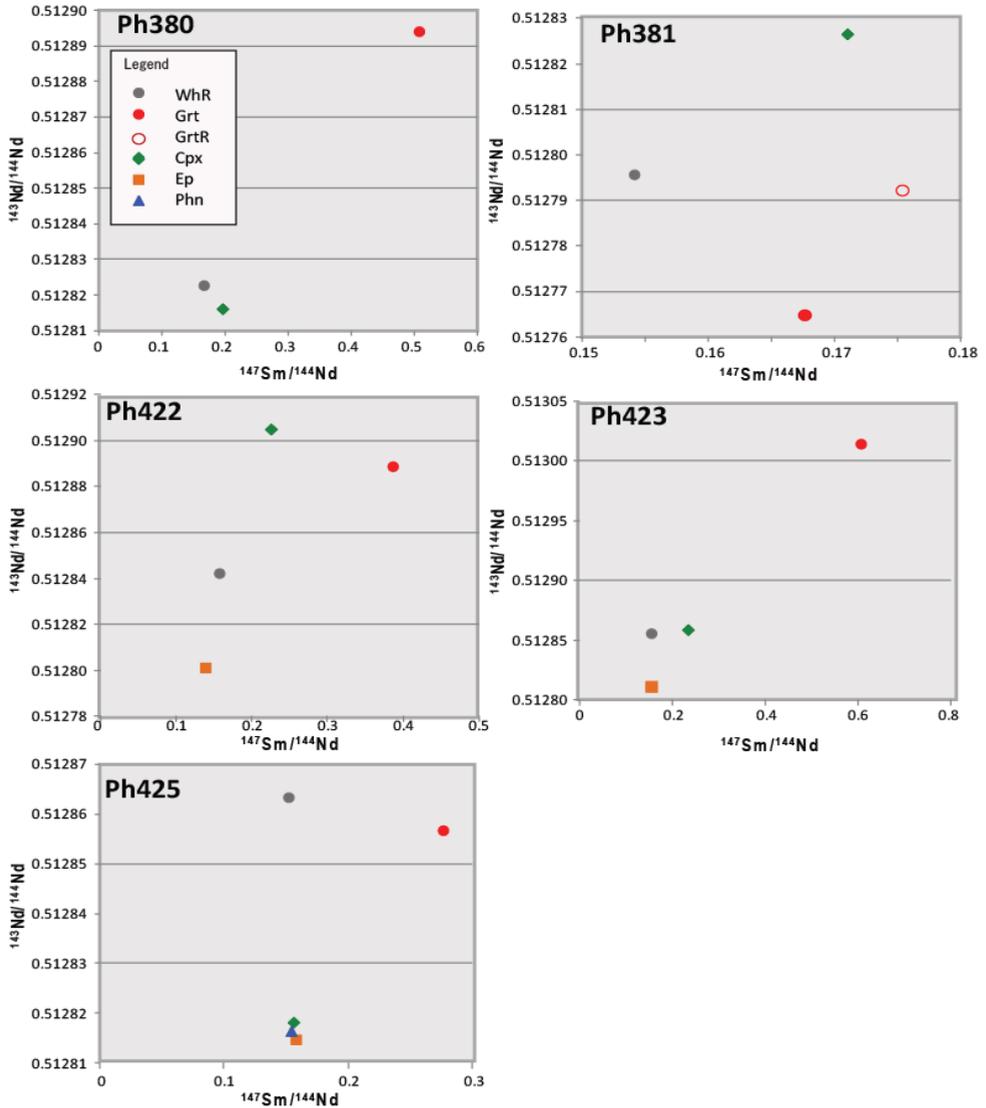


Fig. 5.  $^{147}\text{Sm}/^{144}\text{Nd}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$  diagrams for group I and II ecolites. Samples Ph380 and Ph381 represent Group I, whereas samples Ph422, Ph423, and Ph425 represent Group II ecolites. Abbreviations used are WhR: whole rock, Cpx: clinopyroxene, Ep: epidote, Grt: garnet, and Phn: phengite. GrtR is a repeat analysis of the same garnet fraction. Note the  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of garnet in sample Ph381, and in sample Ph422 which are lower than the ratios of clinopyroxene indicating isotopic disequilibrium for garnet.

The Nd contents in clinopyroxene have intermediate values between those of garnet and whole rock values however, the Sm contents in garnet and clinopyroxene are almost same. The resulting  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios vary from 0.1650 in whole rock to 0.1914 in clinopyroxene to 0.5077 in garnet, whereas the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios range from 0.512816 in clinopyroxene to 0.512823 in whole rock to 0.512894 in garnet. Clinopyroxene and whole rock have somewhat similar  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios however the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in clinopyroxene are slightly lower than those in whole rock (Fig. 5), and garnet has the highest  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. The isotopic data plot in a regression line with a positive slope. Although, three-point isochron cannot be calculated, however the garnet-clinopyroxene pair resulted in an isochron with age value of  $37.9 \pm 6.2$  Ma (Fig. 6a).

In sample Ph381 the Nd contents are 12.18 ppm in garnet, 16.18 ppm in clinopyroxene and 73.79 ppm in whole rock. The Sm contents are 3.37 ppm in garnet, 4.58 ppm in clinopyroxene and 18.81 ppm in whole rock. In this sample also the Nd contents in clinopyroxene have intermediate values between those of garnet and whole rock values. The resulting  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios vary from 0.1542 in whole rock to 0.1711 in clinopyroxene to 0.1677 in garnet, whereas the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios range from 0.512827 in clinopyroxene to 0.512796 in whole rock to 0.512765 in garnet (Fig. 5). Clinopyroxene has highest  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, whereas garnet has the highest  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios exhibits the lowest  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. These results in a regression line with a negative slope, no isochron can be calculated among whole rock and mineral pairs. However, when we calculated all data points of Group I, an isochron or regression line with a  $42 \pm 29$  Ma was constructed (Fig. 6b).

### 5.1.2 Group II eclogites

Similar to Group I eclogites we also analysed Sm and Nd contents,  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios from the whole rock eclogites of Group II (Sample Ph422, Ph423, and Ph425) and their constituent minerals (garnet, clinopyroxene, phengite, and epidote). Results are plotted in Fig. 5 and are shown in Table 1.

In sample Ph422 the Nd contents are 1.49 ppm in garnet, 1.39 ppm in clinopyroxene, 2.26 in phengite and 19.88 ppm in whole rock. The Sm contents are 0.95 ppm in garnet, 0.52 ppm in clinopyroxene, 0.66 ppm in phengite and 5.19 ppm in whole rock. The Nd and Sm contents in epidote in this sample are extremely high i.e. Nd contents are 565 ppm and Sm contents are 129 ppm. The resulting  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios range from 0.1579 in whole rock to 0.2266 in clinopyroxene to 0.1761 in phengite to 0.3856 in garnet, whereas the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios range from 0.512905 in clinopyroxene to 0.512843 in whole rock to 0.512801 in phengite to 0.512889 in garnet. In this sample also, garnet has lower  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios than clinopyroxene (Fig. 5) and results in a regression line with negative slope, thus no isochron can be defined.

In sample Ph423 the Nd contents are 0.51 ppm in garnet, 0.70 ppm in clinopyroxene and 16.87 ppm in whole rock. The Sm contents are 0.51 ppm in garnet, 0.27 ppm in clinopyroxene and 4.24 ppm in whole rock. The Nd and Sm contents in Epidote in this sample are also high i.e. Nd contents are 374 ppm and Sm contents are 95 ppm. The resulting  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios range from 0.1521 in whole rock to 0.2318 in clinopyroxene to

0.6045 in garnet, whereas the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios range from 0.512859 in clinopyroxene to 0.512857 in whole rock to 0.513 in garnet. Whole rock, clinopyroxene and garnet show a large range in  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios with garnet having the highest  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios (Fig. 5). Three-point isochron yields no geological meaningful age. However the regression line drawn from the garnet-whole rock pair plots with a positive slope and gives an isochron of  $53 \pm 14$  Ma.

Sample No.	$^{147}\text{Sm}/^{144}\text{Nd}$	$2\delta(\text{m})$	$^{143}\text{Nd}/^{144}\text{Nd}$	$2\delta(\text{m})$	Nd (ppm)	Sm (ppm)	Sm/Nd
<b>Group I eclogites</b>							
Ph380WhR	0.1650	0.0007	0.512823	6.33E-06	39.77	10.85	0.27
Ph380Grt	0.5077	0.0007	0.512894	9.72E-06	04.69	03.93	0.84
Ph380Cpx	0.1914	0.0014	0.512816	8.64E-06	10.99	03.48	0.32
Ph381WhR	0.1542	0.0005	0.512796	6.47E-06	73.79	18.81	0.25
Ph381Grt	0.1677	0.0019	0.512765	1.09E-05	12.17	03.37	0.28
Ph381Grtr	0.1754	0.0017	0.512792	8.35E-06	12.18	03.53	0.29
Ph381Cpx	0.1711	0.0007	0.512827	5.92E-06	16.18	04.58	0.28
<b>Group II eclogites</b>							
Ph422WhR	0.1579	0.0011	0.512843	7.93E-06	19.88	5.19	0.26
Ph422Grt	0.3856	0.0009	0.512889	7.80E-06	1.49	0.95	0.64
Ph422Cpx	0.2266	0.0008	0.512905	4.55E-05	1.39	0.52	0.37
Ph422Ep	0.1381	0.0006	0.512801	6.76E-06	565	129	0.23
Ph422Phn	0.1761	0.0011	0.512837	8.21E-06	2.26	0.66	0.29
Ph423WhR	0.1521	0.0010	0.512857	8.00E-06	16.87	4.24	0.25
Ph423Grt	0.6045	0.0005	0.513014	4.13E-05	0.51	0.51	1.00
Ph423Cpx	0.2318	0.0008	0.512859	2.38E-05	0.70	0.27	0.38
Ph423Ep	0.1542	0.0017	0.512812	8.88E-06	375	95	0.25
Ph425WhR	0.1522	0.0008	0.512863	7.08E-06	20.64	5.19	0.25
Ph425Grt	0.2780	0.0007	0.512857	1.41E-05	0.62	0.28	0.46
Ph425Cpx	0.1562	0.0009	0.512818	1.64E-05	1.27	0.33	0.26
Ph425Ep	0.1573	0.0008	0.512815	6.71E-06	156	41	0.26
Ph425Phn	0.1550	0.0006	0.512816	1.12E-05	7.37	1.89	0.26

Table 1. Sm-Nd concentrations and isotopic ratios of the whole rock Group I and II eclogites and their constituent minerals. Mineral abbreviations used in the table are same as shown in Fig. 5.

In sample Ph425 the Nd and Sm contents are in the same range as discussed above. The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios range from 0.1522 in whole rock to 0.1562 in clinopyroxene to 0.1550 in phengite to 0.1573 in epidote to 0.2780 in garnet, whereas the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios range from 0.512818 in clinopyroxene to 0.512863 in whole rock to 0.512816 in phengite to 0.512815 in epidote to 0.512857 in garnet (Fig. 5). A three-point isochron (garnet-clinopyroxene-phengite) can be defined with an age values of  $50 \pm 21$  Ma (Fig. 6c). When we pooled all the Sm-Nd data for whole rock and minerals from both groups of eclogites for isochron calculation, we obtained an internal isochron of  $51 \pm 18$  Ma (Fig. 6d).

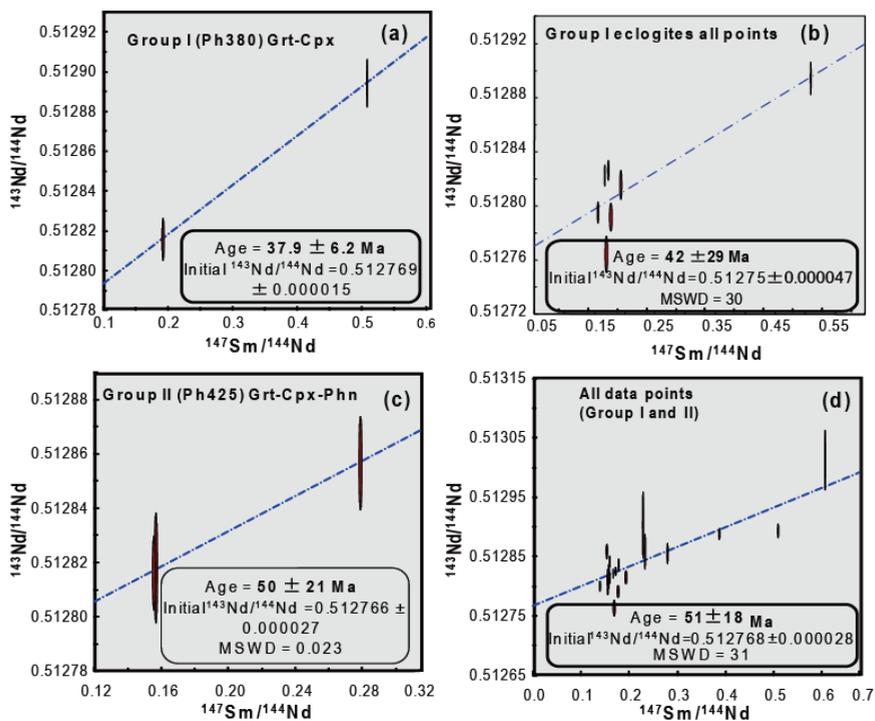


Fig. 6. Sm-Nd isochrones (mixing lines) for the Himalayan Group I and II eclogites. Plots a and b show data from Group I eclogites. Plot c shows three-point isochron from Group II eclogite (sample Ph425). Plot d shows combination of all data pooled as a single system. Data-point error ellipses are  $2\sigma$ . Isochrones were calculated using Isoplot 3.6 (Ludwig, 2009).

## 5.2 Lu-Hf isotope geochemistry

The same five eclogitic whole rock samples and their constituent minerals (garnet, clinopyroxene and epidote) were analyzed for Lu and Hf contents, and  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios (Table 2). Phengite was not analyzed because of its extremely low Hf concentrations. The whole rock samples and separated minerals show large variation in Lu and Hf concentration and Lu/Hf ratio for separated minerals (Table 2).

### 5.2.1 Group I eclogites

Lu and Hf contents,  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios for the whole rock eclogites (Sample Ph380 and Ph381) and for garnet and clinopyroxene from the above two samples have been analysed. Results are plotted in Fig. 7 and are shown in Table 2.

Sample No.	$^{176}\text{Lu}/^{177}\text{Hf}$	$2\delta(\text{m})$	$^{176}\text{Hf}/^{177}\text{Hf}$ corrected	$2\delta(\text{m})$	Lu (ppm)	Hf (ppm)	Lu/Hf
<b>Group I eclogites</b>							
Ph380WhR	0.005532	2.8E-06	0.282844	4.69E-06	0.67	17.22	0.04
Ph380Grt	0.404834	2.0E-04	0.283273	1.22E-05	1.33	0.47	2.85
Ph380Cpx	0.004485	2.2E-06	0.282895	5.05E-06	0.06	1.90	0.03
Ph381WhR	0.008481	4.2E-06	0.282871	3.70E-06	0.78	13.13	0.06
Ph381Grt	0.095139	4.8E-05	0.282944	5.25E-06	1.93	2.89	0.67
Ph381Cpx	0.007200	3.6E-06	0.282908	6.35E-06	0.22	4.37	0.05
Ph381Cpxr	0.007055	3.5E-06	0.282898	3.38E-06	0.22	4.46	0.05
<b>Group II eclogites</b>							
Ph422WhR	0.011174	5.6E-06	0.282898	7.03E-06	0.28	3.52	0.08
Ph422Grt	0.024751	1.2E-05	0.282925	1.34E-05	0.67	3.82	0.17
Ph422Cpx	0.003276	1.6E-06	0.282902	6.64E-06	0.04	1.89	0.02
Ph422Ep	0.008019	4.0E-06	0.282847	1.68E-05	0.14	2.57	0.06
Ph423WhR	0.010787	5.4E-06	0.282900	8.96E-06	0.32	4.25	0.08
Ph423Grt	0.032721	1.6E-05	0.282917	5.30E-06	0.70	3.05	0.23
Ph423Cpx	0.002681	1.3E-06	0.282905	5.76E-06	0.04	1.94	0.02
Ph423Ep	0.030260	1.5E-05	0.282764	4.99E-05	0.12	0.58	0.21
Ph425WhR	0.010889	5.4E-06	0.282909	7.63E-06	0.33	4.27	0.08
Ph425Grt	0.035713	1.8E-05	0.282927	4.96E-06	0.72	2.86	0.25
Ph425Cpx	0.001502	7.5E-07	0.282900	6.21E-06	0.02	1.91	0.01
Ph425Ep	0.023419	1.2E-05	0.282970	3.51E-05	0.09	0.55	0.16

Table 2. Lu-Hf concentrations and isotopic ratios of the whole rock Group I and II eclogites and their constituent minerals. Mineral abbreviations are same as explained earlier.

In sample Ph380 the Lu and Hf contents range from 1.33 ppm in garnet, 0.06 ppm in clinopyroxene to 0.67 ppm in whole rock, respectively, and 0.47 ppm in garnet, 1.90 ppm in clinopyroxene to 17.22 ppm in whole rock, respectively. The resulting  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios vary from 0.005532 in whole rock to 0.004485 in clinopyroxene to 0.404834 in garnet, whereas the  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios range from 0.282895 in clinopyroxene to 0.282844 in whole rock to 0.283273 in garnet. The  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios in whole rock and clinopyroxene have almost same values however with different  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios as shown in Fig. 7 and it is difficult to have a three-point isochron for them. However, a two point mixing line (garnet-clinopyroxene) from this sample defines a slope of  $50.6 \pm 1.7$  Ma (Fig. 8a).

In sample Ph381 the Lu and Hf contents range from 1.93 ppm in garnet, 0.22 ppm in clinopyroxene to 0.78 ppm in whole rock, respectively, and 2.89 ppm in garnet, 4.46 ppm in clinopyroxene to 13.13 ppm in whole rock, respectively. The resulting  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios are 0.008481 in whole rock, 0.0072 in clinopyroxene, and 0.095139 in garnet, whereas the

$^{176}\text{Hf}/^{177}\text{Hf}$  ratios are 0.282908 in clinopyroxene, 0.282871 in whole rock, and 0.282944 in garnet. Same pattern of the isotopic ratios were observed in this sample i.e. similar  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios in whole rock and clinopyroxene (even we repeated analysis for clinopyroxene) and lower  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios in whole rock and slightly higher in clinopyroxene (Fig. 7). Garnet from this sample with considerably high Lu/Hf ratio ( $> 2$ ) yielded a two-point (garnet-whole rock) isochron of  $45.3 \pm 3.9$  Ma (Fig. 8b). However, when data for three points (garnet-whole-rock-clinopyroxene) were used, no isochron was obtained.

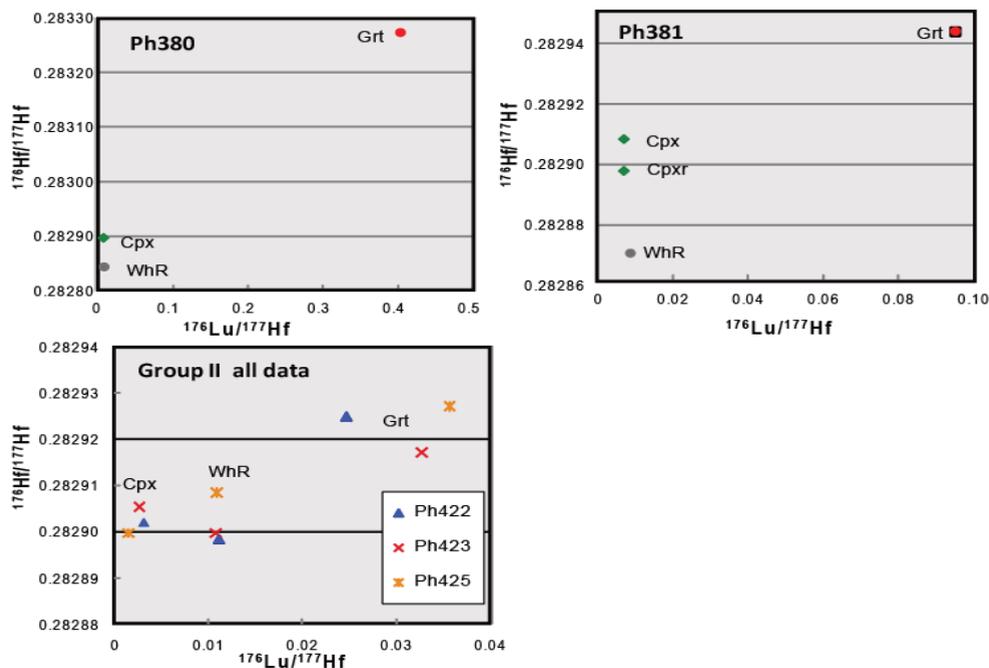


Fig. 7.  $^{176}\text{Lu}/^{177}\text{Hf}$  versus  $^{176}\text{Hf}/^{177}\text{Hf}$  diagrams for group I and II eclogites. Samples Ph380 and Ph381 represent Group I and the lower diagram represents a combined data from the three samples (Ph422, Ph423, and Ph425) of Group II eclogites. Abbreviations used are same as explained above.

### 5.2.2 Group II eclogites

In sample Ph422 the Lu and Hf contents range from 0.67 ppm in garnet, 0.04 ppm in clinopyroxene, 0.14 ppm in epidote to 0.28 ppm in whole rock, respectively, and 3.82 ppm in garnet, 1.89 ppm in clinopyroxene, 2.57 ppm in epidote to 3.52 ppm in whole rock, respectively. The resulting  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios are 0.011174 in whole rock, 0.003276 in clinopyroxene, 0.008019 in epidote, and 0.024751 in garnet, whereas the  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios are 0.282902 in clinopyroxene, 0.282898 in whole rock, 0.282847 in epidote, and 0.282925 in garnet.

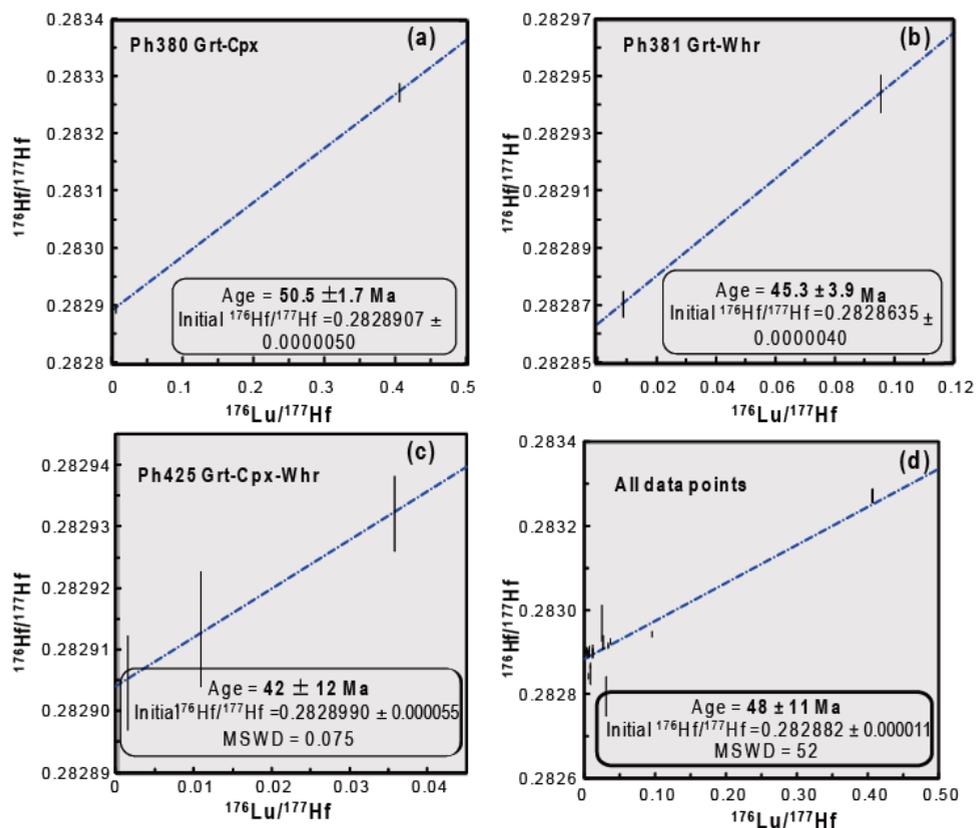


Fig. 8. Lu-Hf garnet-clinopyroxene (a), garnet-whole rock (b), and garnet-clinopyroxene-whole rock isochrones (c) for the Himalayan Group I and II eclogites. Plots a-b show data from Group I eclogites and plot c represents data from one sample in Group II eclogites. Plot d displays combined result for all data and yielded an internal isochron of  $48 \pm 11$  Ma. Data-point error ellipses are  $2\sigma$ . Isochrones were calculated using Isoplot 3.6 (Ludwig, 2009).

Similar results (Lu and Hf contents, and  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios) were observed in other samples of Group II eclogites (i.e. sample Ph423 and Ph425). The whole rock Lu/Hf ratio from Group II eclogites are very much identical, thus, may indicate complete isotopic equilibration, however, the separated minerals show large scatter in Lu/Hf ratio, as well as, in the  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  isotope results (Table 2 and Fig. 7). Garnet from Group II eclogites bears very low Lu/Hf ratio ( $< 3$ ) which may indicate isotopic disequilibrium or the effect of micro-inclusions. When various data points (garnet-clinopyroxene, garnet-whole rock or garnet-whole rock-clinopyroxene) were used to calculate isochrones, the age values obtained from these mixing lines show an age range between 50 and 30 Ma. In contrast when we utilised the Lu-Hf data of sample Ph425 (fresh eclogite) for three-point isochron (garnet-clinopyroxene-whole rock), an age value of  $42 \pm 12$  Ma (with smaller values of MSWD: 0.075) was obtained (Fig. 8c). Since, the Himalayan eclogites of the Kaghan Valley are derived from the Panjal Trap volcanics and they were metamorphosed during the

subduction of the Indian Plate slab beneath the Asian Plate, therefore, we could pool all the analysed samples (whole rock and separated minerals as a single system) and an internal isochron of  $48 \pm 11$  Ma (MSWD=52) was obtained (Fig. 8d). These results are consistent with the previously reported Sm-Nd isochron results for the Kaghan Valley eclogites by Tonarini et al. (1993).

## 6. Interpretation of results

### 6.1 Multistage mixing

The Rb-Sr isotope results (Spencer et al., 1995) and Sm-Nd isotopic results (this study) from the whole rock did not yield isochron, however, in situ zircon U-Pb isotope yielded age values between 254 and 267 Ma (Spencer & Gebauer 1996; Parrish et al., 2006; Rehman et al., 2010; Wilke et al., 2010a) show evidence of magmatic activity in Permian. From the available reference data and the present results of multi-isotope systems, we interpret that the Himalayan eclogites were originated from a wide range magmatic activity throughout the Himalayan region in the Permian to Carboniferous time. The eclogites found as lenses and sheets in the Kaghan Valley indicate Panjal Trap basaltic volcanism and intrusive diking. The presence of abundant zircons and the Fe-Ti rich chemical composition of Group I eclogites (Rehman et al., 2008) indicate probably a gabbroic protolith for some of these eclogites. The large time span from the initiation of volcanic activity in the Permian (ca. 267 Ma to 254 Ma; obtained from the protolith-related zircon U-Pb age-dating by Rehman et al 2010) to the subduction-related metamorphism in the Eocene (ca. 50 to 40 Ma; obtained from the Sm-Nd and Lu-Hf isotopes during this study, and the U-Pb zircon age-dating from felsic gneisses which surround these eclogites by Kaneko et al., 2003) reveal multistage mixing of these eclogites. The volcanic activity started primarily at 267 Ma followed by the probable mixing of the sediment component during magmatic assimilation and periodic volcanic events in the later stages as indicated by the U-Pb zircon ages (Rehman et al. 2008).

Furthermore, the India-Asia collision before and after 50 Ma and the subduction-related metamorphic event between 50 and 40 Ma suggest an open system where elemental exchange occurred when the Indian Plate slab was subducting to mantle depths. The whole rock  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios from selected eclogite samples when used for internal isochron yielded an isochron of  $569 \pm 180$  Ma (MSWD = 3.4), rather defines a mixing line and hence giving values older than the protolith age. This result indicates that a crustal component (most probably sediment flux) incorporated in the eclogite source rock.

Moreover, the  $\epsilon\text{Nd}$  verses  $\epsilon\text{Hf}$  plot for the Kaghan Valley eclogites (Fig. 9) also indicates that these eclogites were derived from ocean-island-basalts with a significant mixing trend of sediments component (as shown in Fig. 9 with  $\epsilon$  (t 267, t 46, and t 0). The large variations in the Sm-Nd isotope ratios strongly suggest that the precursor rocks of these eclogites assimilated a sediment component during volcanic activity with further possible fluid influx during subduction of the Indian Plate slab after it's collision with the Asian Plate.

### 6.2 Low Sm/Nd and Lu/Hf ratios: Effect of inherited micro-inclusions

The use of separated or in situ minerals (e.g. garnet, clinopyroxene, phengite, zircon, monazite, and hornblende etc.) as a chronometer, mostly provides exact time information of history of the rocks, however, the strong preference of the garnet lattice for the heavy rare

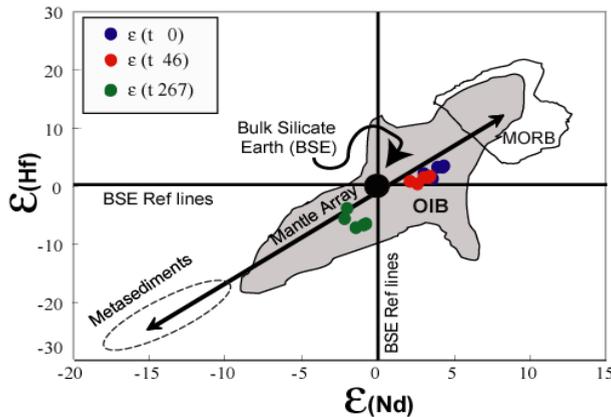


Fig. 9. Plot displaying the Hf-Nd isotopic compositions of the Himalayan eclogites at 267 Ma (protolith age; green circles), at 46 Ma (UHP eclogite facies metamorphic stage; red circles), and at 0 Ma (present time; blue circles) relative to the terrestrial Hf-Nd mantle array. Fields for the mid-ocean-ridge-basalts (MORB) and ocean-island-basalts (OIB) are modified from John et al. (2004) and references therein. Field for metasediments was adopted from Kempton et al. (2002). Bulk Silicate Earth (BSE) is assumed to be chondritic with respect to Lu-Hf and Sm-Nd.

earth elements over light rare earth elements makes this mineral highly suitable for Sm-Nd dating (relatively less mobile) (Thöni, 2002). Moreover, the Lu-Hf system (relatively immobile) has been argued to be superior to the Sm-Nd method in some respects (e.g. Blichert-Toft et al., 1999; Blichert-Toft & Frei, 2001; de Sigoyer et al., 2000). Particularly, the immobile nature of the Lu-Hf dating (Blichert-Toft et al., 1999; White, 2009) is considered to be the best used for metamorphic rocks. When applying Sm-Nd and Lu-Hf isotope systems, using separated minerals, for geochronological research, the problem of the influence of high-light rare earth element inclusions is strong (Thöni, 2002).

In case of the Kaghan Valley eclogites (both Group I and II) it is clear that the above factor played a vital role. The possible presence of micro-inclusion (zircon and/or allanite?) even in the optically clean mineral separates could have affected the isotopic ratios. Also, the very low Sm/Nd ratio ( $< 0.6$ ) and Lu/Hf ratio ( $< 0.3$ ) and concentration in garnet and the negative correlation of Sm-Nd isotope ratios (Fig. 5) in garnet and clinopyroxene in sample Ph381 (Group I eclogites) indicate abnormal behaviour which caused the isotopic disequilibrium. That is why no isochron relationship was constructed between garnet and clinopyroxene or garnet and whole rock. Even if an isochron was calculated for a single pair (i.e. garnet-clinopyroxene) a two-point mixing line was always obtained with more or less identical age values for the metamorphic event the Himalayan eclogites have experienced. However, a two-point isochron calculation may not always yield geologically meaningful ages. Same pattern is observed in the present research. The age values obtained from various mineral-mineral pairs and mineral-whole rock pairs fall in the metamorphic age range for the Himalayan eclogite facies event but the scatter in age values and the errors are large. This scatter in isochrones/mixing lines and their large errors or no isochron relationship among various minerals indicate presence of optically invisible micro-

inclusions, which could have disturbed the concentrations of the heavy rare earth elements over light rare earth elements. In contrast, for samples having no effect of micro-inclusions, a three-point isochron was obtained which yielded geologically meaningful age (Fig. 6c) if we assume that the isotopic equilibrium was reached in those samples.

### 6.3 Isotopic disequilibrium

Rocks under eclogite facies conditions usually show disequilibrium amongst major and trace elements and therefore isotopic systems very often do not remain in equilibrium (Vidal & Hunziker, 1985). The Kaghan Valley eclogites display large variations in major and trace element geochemistry (Rehman et al., 2008), and are in partial disequilibrium; for example Rb-Sr (Spencer et al., 1995) and Sm-Nd (Samples Ph381 and Ph422; this study). In the work of Spencer et al. (1995; Fig. 4, p. 98), it is clear that the analyzed eclogite samples align poorly along the reference isochron of 270 Ma. This indicates (i) either an addition of a crustal component to the protolith after their emplacement but before their subduction or (ii) a fluid infiltration to the eclogite protolith during the subduction of the Indian Plate slab. Moreover, additional remobilization of trace elements and rare earth elements must have occurred to produce the observed isotopic disequilibrium during eclogite facies metamorphism and late-stage retrogression. The isotopic disequilibrium can be seen in two of the eclogite samples (Ph381:Group I, and Ph422; Group II) in which garnet show either  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios lower than the whole rock or  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios lower than whole rock for higher  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios (Fig. 5). Also, it is important to note that the timing of eclogite facies metamorphism at 49 Ma (Tonarini et al., 1993) was adopted from a single garnet-clinopyroxene pair of the two analyzed samples, a second garnet-clinopyroxene pair (sample 90/181 of Tonarini et al., 1993) resulted in an isochron of  $89 \pm 4$  Ma. This implies that the Sm and Nd, and presumably other trace elements underwent remobilization during subduction of the eclogite protolith, and/or later fluid infiltration, resulting in incomplete equilibration.

The reason for disequilibrium can be the incomplete recrystallization of garnet either during an UHP eclogite facies event or during retrogression (Mørk & Mearns, 1986; Luais, et al., 2001). The Sm-Nd mineral equilibria of eclogites have been used to estimate a Sm-Nd closure temperature of 600–800 °C in garnets from various tectonic settings (Mezger et al., 1992; Hensen & Zhou, 1995; Luais et al., 2001). The Himalayan eclogites of the Kaghan Valley have a temperature range of 650–780 °C, within the closure temperature range for the Sm-Nd isotopic system. However, due to an amphibolite facies overprint and subsequent retrogression, volume diffusion or elemental remobilization might have occurred under fluid-rich conditions, resulting in isotopic disequilibrium. Garnet crystallizes partly from pre-existing plagioclase, with contrasting rare earth element patterns (low Sm/Nd ratio of 0.2). This reaction implies the transfer of major elements between igneous and metamorphic minerals. The isotopic ratio of the plagioclase could be preserved during garnet growth, provided that trace elements such as rare earth elements are less mobile than major elements during mineral reactions (Luais et al., 2001). The high Sm/Nd ratio of 1.25 in garnet from sample Ph381Grt is in disequilibrium, compared to the low Sm/Nd ratios of 0.37 in garnet from sample Ph425Grt, and Sm/Nd ratios of 0.79 in garnet from sample Ph380Grt, which is in equilibrium (See table 1 for sample numbers). Our data indicate that the garnets are in disequilibrium, as reflected by the extremely low  $^{143}\text{Nd}/^{147}\text{Nd}$  ratios, variable Sm and Nd

concentrations, and negative correlation (Fig. 5), thus no isochron was defined. Similarly, low Lu/Hf ratios ( $< 0.3$ ) and concentrations in garnets also support our conclusion of isotopic disequilibrium even in the case of immobile elements. Therefore, several mineral-mineral pairs and mineral-whole rock pairs when applied for Lu-Hf isochron calculations, no geologically meaningful age was obtained. However when all data was pooled as one system, an internal isochron with identical age values representing the Himalayan eclogite facies event was obtained (Fig. 8d).

## 7. Conclusion

1. Eclogites from the Himalayan mountain chain (Kaghan Valley) are classified into two groups on the basis of field occurrence, petrology, and multi-isotope data. Group I eclogites are massive and they record high-pressure metamorphism. Group II eclogites appear as thin lenses or boudines, and they record ultrahigh-pressure metamorphism.
2. Their geochemical characteristics (Sm-Nd and Lu-Hf isotope ratios) are fairly similar to within-plate-basalts or ocean-island-basalts. The U-Pb zircon age dating (254 ~ 267 Ma) from the protolith-related magmatic zircons indicate that the magmatic activity occurred in Permian when the Panjal Trap basalts were extruded. Thus during their extrusion a significant sediment component mixing could have occurred, that is why the initial  $\epsilon\text{Nd}$  versus  $\epsilon\text{Hf}$  values shows the composition of eclogite protolith (at t 267 Ma) close to the metasediments field. Our results of multi-isotope systems indicate that the Himalayan eclogites were probably originated from a wide range magmatic activity in which a sediment component mixed significantly. Moreover, the Fe-Ti enriched pattern and the presence of abundant magmatic zircons in Group II eclogites indicate probably a gabbroic protolith for some of these eclogites. In contrast, the lens- or boudine-type Group II eclogites were derived from basaltic volcanism with some intrusive diking.
3. The Sm-Nd and Lu-Hf isotope systems applied for the Kaghan Valley eclogites did not yield isochron age for the whole rock samples. However, the calculated isochrones from various mineral-mineral and mineral-whole rock pairs exhibited slightly different results. Group II eclogites have higher  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, and lower Sm-Nd concentrations. The Sm and Nd concentration and Sm/Nd ratio among same minerals but in different samples with contrasting differences indicates that even optically clean mineral separates, particularly garnet, may contain high-light rare earth element micro-inclusions such as allanite, epidote/zoisite, apatite or zircon. Therefore, the extremely low concentrations and low Sm/Nd ratios in garnet from Group II eclogite are probably controlled by the presence of allanite/epidote micro-inclusions. The Sm-Nd mixing lines show values ranging from 51 Ma to 38 Ma, using two- to three-point isochrones. Some of the pseudo-isochrones gave values close to those which were published by earlier workers. The Sm-Nd data from all five whole rock samples and their constituent minerals defined an internal isochron of  $51 \pm 18$  Ma, which is consistent with the previous results but with large error and a large value of MSWD.
4. Multi-isotope ratios and compositions from both whole-rocks and their constituent minerals indicate considerable trace element mobilization during subduction of the Indian Plate. The large scatter in Sm-Nd and Lu-Hf isotopic ratios in same minerals of different samples and the large difference in isochron/mixing lines within same group eclogites in this and previous studies indicate that the Sm-Nd and Lu-Hf isotope

systems experienced remobilization with other trace elements during their subduction to deeper crustal levels. In addition, they may have been disturbed by later fluid infiltration that produced isotopic disequilibrium among some rock samples.

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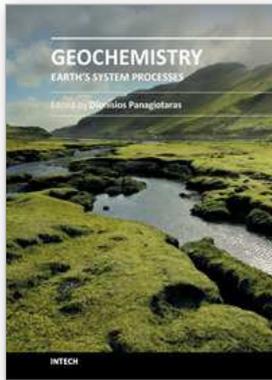
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This book brings together the knowledge from a variety of topics within the field of geochemistry. The audience for this book consists of a multitude of scientists such as physicists, geologists, technologists, petroleum engineers, volcanologists, geochemists and government agencies. The topics represented facilitate as establishing a starting point for new ideas and further contributions. An effective management of geological and environmental issues requires the understanding of recent research in minerals, soil, ores, rocks, water, sediments. The use of geostatistical and geochemical methods relies heavily on the extraction of this book. The research presented was carried out by experts and is therefore highly recommended to scientists, under- and post-graduate students who want to gain knowledge about the recent developments in geochemistry and benefit from an enhanced understanding of the dynamics of the earth's system processes.

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