The applications of the $^{187}$Re-$^{187}$Os isotope pair as a petrogenetic and geologic tracer are increasing in recent years due to several advances in the chemical extraction and purification of Re and Os, occurring at ppb levels in environmental samples, and in the precise determination of the Os isotope composition. We have established in our laboratory, based on available methods, chemical procedures and Negative Thermal Ionisation Mass Spectrometric techniques for the measurement of Re-Os concentrations in environmental samples and the Os isotope composition in them. Using these techniques, we are able to determine $^{187}$Os/$^{186}$Os ratios with a precision of ~ 1% ($\pm 2 \sigma$, twice the standard error of the mean) in several tens of picogram of Os. Preliminary analysis of black shales from the Lower Tal section of the Maldeota phosphorite mine yields a mean $^{187}$Re-$^{187}$Os model age of 597 ± 30 Ma. The $^{187}$Os/$^{186}$Os and Os concentration in black shales of the Lesser Himalaya range from 8 to 96 and 0.02 to 13 ng g$^{-1}$ respectively. The mean $^{187}$Os/$^{186}$Os in these samples is ~ 25, significantly higher than the crustal value of ~ 10.5, suggesting that these black shales could be an important source of radiogenic Os to the rivers draining the Himalaya and to the steady increase in $^{187}$Os/$^{186}$Os of the oceans through the Cenozoic.

1. Introduction

The chronometric and tracer applications of the $^{187}$Re-$^{187}$Os isotope pair in Earth and Planetary systems are getting increasingly recognised. The precise measurement of Re and Os concentrations and Os isotope composition in terrestrial and extraterrestrial samples by secondary ion mass spectrometry, SIMS (Allegre and Luck 1980; Luck et al. 1980; Luck and Allegre 1983) facilitated the applications of the Re-Os decay scheme in geology, geochemistry and cosmochemistry. These studies got a further boost, during the past few years, with the development of the Negative Thermal Ionisation Mass Spectrometry (NTIMS) technique for the precise determination of Re and Os concentrations and Os isotopic composition in very small samples, several tens to a few hundreds of picograms (Creaser et al. 1991; Volkening et al. 1991; Hauri and Hart 1993). In this paper, we document the establishment of techniques for the extraction and measurement of Re-Os isotopes from environmental samples in our laboratory based on available methods. These techniques, established for the first time in India, have been used to analyse a variety of environmental samples for their Re-Os isotope systematics. Some of these results from the sedimentaries of the Lesser Himalaya, specifically those on the black shales, are presented in this paper. Our studies on black shales are motivated by two considerations: (i) to explore the possibility of using the $^{187}$Re-$^{187}$Os pair to determine their chronology (Ravizza and Turekian 1989) and look for age correlation between the inner and outer belt sedimentary sequences and (ii) to assess their potential to contribute radiogenic Os to the oceans and thereby to the marine Os isotope evolution (Pegram et al. 1992; Ravizza 1993; Ehrenbrink et al. 1995). Weathering of black shales, which are generally rich in Re and Os (Ravizza 1991), from the Himalaya has been suggested as a source for the steady increase in oceanic $^{187}$Os/$^{186}$Os during the Cenozoic (Pegram et al. 1992; Ehrenbrink et al. 1995; Turekian and Pegram 1997). A reconnaissance survey of Os isotope composition of black shales from the Lesser Himalaya was initiated as a part of this study to determine the range of Os concentration and $^{187}$Os/$^{186}$Os in them.

Keywords. Re-Os isotopes; Himalaya; black shales; chronology.
2. Analytical techniques

Os and Re abundances in geological and environmental samples are quite low, typically of the order of a few tens of picograms to nanograms per gram. Precise determination of Os and Re concentrations in these samples and their Os isotopic composition, therefore, requires the extraction and purification of subnanogram to nanogram quantities of these metals from several grams of samples.

2.1 Re, Os standards, spikes and reagents

The Re and Os standards and spikes used for calibration and standardisation of mass spectrometric procedures and the determination of Re and Os concentrations were provided by G. Ravizza (Woods Hole Oceanographic Institution, USA) and W. Pegram (Yale University, USA). The Os standard solution is a specpure solution of (NH₄)₂OsCl₆ in 6N HCl (Esser 1991). The Os spike solution is enriched in 190Os with an isotopic composition of 96.6% 190Os, 1.9% 192Os, 1.0% 189Os, 0.5% 188Os and < 0.1% 187Os (Esser 1991). The Re standard is a nitric acid solution of 99.999% potassium perrhenate. The Re spike is an acid solution of enriched Re metal (94.5% 185Re; Ravizza 1991). These standards and spikes were suitably diluted using appropriate high purity acids and their strengths were mutually calibrated (Singh 1999).

The need to extract and purify subnanogram to nanogram quantities of Os and Re from various samples places stringent requirements on the purity of reagents and cleanliness of glass and Teflon wares used for the analysis as the procedural blank levels have to be extremely low, less than a few picograms. The acids, H₂SO₄, HNO₃ and HBr were procured from SeaStar laboratories were procured mainly from Savillex Corporation, USA. They were first cleaned in Milli-Q water and finally with QD H₂O. Teflon wares were procured mainly from Savillex Corporation, USA. They were first cleaned in Milli-Q water and then in hot conc. HNO₃ for 3–4 days. They were then filled with a mixture of HNO₃, HF and H₂O in 2:2:1 ratio, capped, wrapped in transparent cling films and kept under heat lamp for several hours to days. Just prior to use, the acid is emptied, rinsed several times with Milli-Q water and finally with QD H₂O.

2.2 Os Chemistry

Os from various geological samples (black shales, igneous rocks, river and sea sediments) can be extracted either by acid dissolution (Walker 1988; Pegram and Allegre 1992; Shirey and Walker 1995) or by NiS fusion (Esser 1991; Ravizza 1991; Ehrenbrink and Blum 1998). Both these methods have their own merits and disadvantages. For example, the low temperature acid digestion technique is not quite effective for dissolving resistant minerals (e.g. chromitite, magnetite) whereas the high temperature (~ 240°C) Carius tube digestion can result in incomplete dissolution of silicates and organic matter. The advantages of acid digestion techniques are that they generally have lower blanks and allow the determination of both Re and Os in the same sample aliquot. The NiS fire assay technique is suited for the extraction of Os from several grams of geological samples, particularly from organic matter rich samples. Considering this, in this work the NiS fusion technique was used to preconcentrate Os from black shales and other samples though volatile loss of Os (and hence equilibration between sample and spike Os) can potentially be a concern. As will be discussed later, this will be addressed through repeat measurements of Os in separate sample aliquots.

Typically, 0.5–2.0 g of samples were used for Os measurements. Samples were mixed with the fusion flux (Na₂B₄O₇·10H₂O, Na₂CO₃) in the ratio 2:1, Ni (~250 mg) and S (~175 mg) and placed in a porcelain crucible (“Coors”, acquired from Thomas Scientific, USA). After this, Os spike solution was added, the crucible was covered with a lid and placed in a muffle furnace at 800°C. The temperature was raised to ~1080°C and maintained at this temperature for 2–3 hrs. The crucible was allowed to cool and was broken to remove the NiS bead. It was weighed to determine yield, which generally was in the range of 70–90%. The bead was dissolved by refluxing for several hours with distilled HCl in a conical flask. The solution was cooled to room temperature, filtered through a 25 mm dia 0.45 μm Millipore filter to collect the insoluble sulfides which are known to retain Os quantitatively. The filter paper was carefully placed in a precleaned 250 ml distillation flask. About 10 ml conc. H₂SO₄ was added to dissolve the filter paper and then ~80 ml QD H₂O to make the acid strength ~4N (water was added slowly to minimize heating). To this ~3 ml of 4N H₂SO₄ containing ~300 mg CrO₃ was added. The mixture was distilled using purified air as carrier gas following the procedure outlined by Luck (1982) and modified at Yale (Martin 1990). The Os distillate was collected in ~8 ml ice cooled H₂O₂ and further purified by distilling it into ~8 ml HBr. The HBr was transferred to 15 ml Savillex digestion vial, capped and
kept at 80°~100°C overnight. The solution was then slowly evaporated to 0.5 ml on a hot plate, transferred to the cap of the digestion vial and taken to near dryness (~1 μl). This was suitably diluted with QD H2O and Os purified by single bead grain chemistry (Falkner 1992) using Chelex-20 ion exchange resin (20-50 mesh). The purified Os was slowly evaporated to <1 μl and carefully loaded on to a Os-Re free Pt filament (H. Cross Company, USA) using Teflon capillary connected to a microsyringe. Prior to loading, the Pt filament was spot welded on the posts of filament holder and degassed under vacuum (10⁻⁷ torr) at ~900°C (orange red colour) for 3~4 hours.

2.3 Re Chemistry

The NiS fire assay technique used for the extraction of Os is not suitable for Re as it is not quantitatively partitioned into NiS. Therefore, for the determination of Re concentration, samples were bought into solution by acid digestion and Re purified by ion exchange procedure (Ravizza 1991; Shen et al 1996). Thus, in the present study Re and Os were measured in separate aliquots of the sample. For acid digestion, about 0.25~0.5 g of powdered samples were taken in 15/30 ml Savillex digestion vials, wetted with QD H2O and a few drops of conc. HNO3. To this, Re spike was added followed by ~10 ml conc. HNO3. The vessel was sealed and kept at 80°~100°C on a hot plate for ~24 hours after which it was opened to evaporate the HNO3. The residue was digested twice, each time with ~5 ml HF, taken to dryness first with HNO3 and then with aquaregia to bring it to solution. In some samples, particularly black shales from the Himalaya, there was often a small amount of dark residue even after repeated HNO3-aquaregia treatments which interfered with the Re chemistry and mass spectrometry. The Re concentration in these samples, therefore, was measured after ashing them at 450°C~600°C for ~12 hrs. (Colodner et al 1993; Singh 1999) and bringing the ashed sample to solution by acid digestion. The sample solution is brought to dryness, digested with a drop of conc. HNO3, dried and taken in 0.2 N HNO3 (~0.5 gl). A part of this solution is loaded on the filament for mass spectrometric measurements.

2.4 Os and Re mass spectrometry

Isotopic analysis of some of the Pt group elements by NTIMS was pioneered by Heumann (1988) which was later extended to Re, Os and Ir (Creaser et al 1991; Volkening et al 1991; Hauri and Hart 1993). We have established the NTIMS technique at PRL for the measurement of Re and Os isotope composition following the above published procedures. The mass spectrometer used in our studies is an indigenously built, 23 cm radius, 60° sector magnetic field, single focusing instrument equipped with a single faraday collector (Trivedi 1990). This machine was used earlier for Rb-Sr isotopic analyses (Trivedi 1990; Trivedi et al 1995). The polarities of the magnet and ion acceleration high voltage were reversed to suit the NTIMS mode of operation.

The Os fraction loaded on the degassed Pt filament was dried at ~0.5 A current, heated to dull red heat (~600°C) in vacuum (<10⁻⁷ torr) for 8~10 hours to reduce it to Os metal. About 20 μg of specpure Ba(NO3)2 (Spex Industries Inc., USA) as a solution in 0.2 N HNO3 was loaded on the filament for mass spectrometric measurements.
was loaded on top of the Os metal and dried at 0.5 A to enhance the production of negative ions of OsO$_3$ (Creaser et al. 1991). The mass spectrometric measurements of Os (and Re) were carried out by bleeding oxygen into the mass spectrometer at a pressure of $\sim 2 \times 10^{-9}$ torr (Hauri and Hart 1993) to promote ionization efficiency of OsO$_3$ (and ReO$_4$). For calibration, masses 240 ($^{192}$OsO$_3^{160}$O$_3^{180}$), 238 ($^{190}$OsO$_3^{160}$O$_3^{180}$), 237 ($^{188}$OsO$_3^{160}$O$_3^{182}$), 236 ($^{186}$OsO$_3^{160}$O$_3^{182}$), 235 ($^{187}$OsO$_3^{160}$O$_3^{182}$) and 234 ($^{186}$OsO$_3^{160}$O$_3^{180}$) were measured, however in routine analysis only four masses 235, 236, 238 and 240 were recorded. Mass spectra of Os standard solution and Os extracted from one of the black shales are shown in figure 1. The peak heights were measured digitally during peak jumping using an electrometer. Typical ion currents were about $10^{-13}$ A at mass 240 for ~ 100 pg Os load. The peak height at mass 235 ($^{187}$OsO$_3^{160}$O$_3^{182}$) in Os standard (figure 1) is considerably less than that at mass 240 ($^{192}$OsO$_3^{160}$O$_3^{180}$) as the natural abundance of $^{187}$Os (~ 1.5%) is much less compared to that of $^{192}$Os (~ 41%). In Os extracted from black shales, the peak heights at 235 and 240 are generally of similar magnitude (within a factor of ~ 2, figure 1). Backgrounds were measured at masses 233.5 and 240.5. The measured oxide ratios were corrected for instrumental mass fractionation by normalising them to the expected 236/240 ratio (calculated using $^{188}$OsO$_3^{192}$Os = 0.32439, $^{17}$O/$^{16}$O = 0.0003708, $^{18}$O/$^{16}$O = 0.002045, Nier 1937, 1950) and for interferences from oxide ratios typically have ~ 1% standard error of the mean ($\sigma_\mu$). The precision of Os concentration determination, based on counting statistics is ~ 2–3% (±2 s.d.). The difference in Os concentration between duplicates in five pairs of samples average 3% and provides another means to obtain the precision of Os concentration measurement.

Typical ion current for a 100 pg load Re standard was about $5 \times 10^{-13}$ A at mass 251. Currents of Re extracted from samples were lower relative to standard of comparable load probably because of interference from organic matter and/or other ions such as chromate (Shen et al. 1996). Similar to Os data reduction, corrections for oxide interference ($^{185}$ReO$_3^{160}$O$_3^{180}$ on $^{187}$ReO$_4^{160}$O$_7^-$) were made for calculating Re concentration. The Os and Re data reduction procedures followed those being used at Yale and WHOI (Ravizza, Williams pers. comm.).

Table 1 lists the isotopic composition of Os measured in standard. The $^{187}$Os/$^{186}$Os is calculated from the measured $^{187}$Os/$^{192}$Os and using a value of 0.03907 for $^{186}$Os/$^{192}$Os (Luck and Allegre 1983). The results show that the $^{187}$Os/$^{192}$Os and $^{188}$Os/$^{192}$Os in the standard are 0.8884 ± 0.0198 and 0.6443 ± 0.0033, respectively in agreement within errors with those reported (table 1).

The $^{185}$Re/$^{187}$Re ratio in standard is 0.594 ± 0.003, consistent with reported values within errors. The precision of Re concentration measurements (± 2 s.d.) is typically ~ 2–3%. The difference in Re concentration between duplicates in eight pairs of samples range between 0.8 and 4.2% (Singh 1999) with a mean of 2.4% and provides an independent assessment of the precision of Re concentration determination.

2.5 Reproducibility of sample measurements and procedural blanks

Two samples of black shales of known Os and Re concentrations and isotope composition were analysed to check the accuracy and precision of the entire procedure, NiS fusion, wet chemistry and mass spectrometric analysis. These samples were obtained from Dr. G Ravizza and their Os and Re analyses were made earlier by the SIMS technique (Ravizza 1991 and pers. comm.). Table 2 lists the inter-comparison between the two sets of measurements, which shows reasonable agreement. In addition, we also analysed a few samples of black shales from the Lesser Himalaya in duplicate to assess the reproducibility of the measurements. The results (table 3) show that the Os concentration and $^{187}$Os/$^{186}$Os in duplicates are in very good agreement. It can be further inferred from data in tables 2 and 3 that Os from black shales gets well equilibrated with the added spike during fusion and that there is no discernible volatile loss of either Os spike or Os from the sample prior to their equilibration. In these samples Re concentration was measured both by wet oxidation and after ashing. The results (table 3) are consistent with errors suggesting that there is no measurable loss of Re during the ashing process. The consistency in the Os and Re concentrations in the replicates further suggests that they are
homogeneously distributed in these black shales and that their measurement in different sample splits is unlikely to introduce additional uncertainties in the 187Re/186Os ratios.

Three procedural blanks for Os were run for the NiS fusion and wet chemistry using 250–500 mg Ni. The total Os blank for the entire extraction and chemical procedure ranged between 0.8 and 6.1 pg and averaged 2.8 ± 2.9 pg. In addition, one blank for distillation and bead chemistry was measured to be 1.4 ± 0.2 pg Os. An independent assessment of the blank could also be obtained from the analysis of a granite sample, which yielded a total Os signal of 1.87 ± 0.18 pg. All these measurements show that the total Os blank in this study is in the range of 2–3 pg. Os isotopic measurements could not be made on these blanks, as the Os load on the filament was quite low (≤ 1 pg). These blanks are 2–3 orders of magnitude lower than those extracted from many of the black shale samples; but are comparable to those from granites and carbonates (table 4).

We ran four procedural blanks for Re; these ranged from 1.7 to 4.5 pg Re with a mean of 3.5 ± 1.2 pg. As in the case of Os, these represent the total Re blank associated with each analysis. It has been suggested that (Hauri and Hart 1993) Re blank comes mainly from the Pt filament, we, however, have not made any specific attempt to identify the source of Re blank.

3. Re, Os concentrations and Os isotopic composition in samples from the Himalaya

The Re, Os concentrations and Os isotopic composition in some of the samples we have measured from the Himalaya are given in table 4. Reconnaissance study of Os isotopic composition of black shales collected from outcrops in the central and western Lesser Himalaya (Simla, Mussoorie, Nainital and Almora) shows that their 187Os/186Os vary between 8 and 96, with Os concentration ranging from ~ 0.02 ng g⁻¹ to 13 ng g⁻¹ (figure 2; Singh et al. 1998). Among the samples analysed, the smallest Os load on the filament for which isotopic measurements could be made precisely was ~ 20 pg. This Os was extracted from ~ 2 g of black shale (UK94-58) with an Os concentration of ~ 23 pg g⁻¹ (~ 50% chemical efficiency is assumed).

In the area of surficial geochemistry, a topic of considerable interest is the role of Himalayan Orogeny and weathering in contributing to the Os isotope evolution of the oceans. It is well established that 187Os/186Os of the oceans has been increasing since the Cenozoic (Pegram et al. 1992; Ravizza 1993; Ehrenbrink et al. 1995). A suggested cause for this increase is the weathering of black shales which are generally enriched in Os (Ravizza 1991) and hence in 187Os/186Os.

Further, the use of 187Re-187Os pair to date black shales (Ravizza and Turekian 1989) from the inner and outer belts of Himalaya could help in understanding the temporal and spatial relation between them and thereby test tectonic models proposed for their present day occurrence and distribution (Mehr 1977; Valdiya 1995).

There is a lot of debate regarding the absolute ages of Blaini-Krol-Tal successions in the Lesser Himalaya. Studies of trace fossils and small shelly faunas in the phosphorite band of the Tal Formation places this formation in the Early Cambrian and the Krol-Tal boundary as the Precambrian-Cambrian boundary (Azami 1983; Singh and Rai 1983; Shanker et al. 1993). Recently Banerjee et al. (1997) have attempted to
Table 4.  Re, Os concentrations and $^{187}\text{Os}/^{188}\text{Os}$ in samples from the Lesser Himalaya.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Re (ppb)$^a$</th>
<th>Os (ppb)$^b$</th>
<th>$^{187}\text{Re}/^{188}\text{Os}$</th>
<th>$^{187}\text{Re}/^{188}\text{Os}$</th>
<th>$^{187}\text{Os}/^{188}\text{Os}$</th>
<th>$^{187}\text{Os}/^{188}\text{Os}$</th>
<th>Model age$^c$(Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Shale</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KU92-2</td>
<td>Almora</td>
<td>–</td>
<td>0.04</td>
<td>–</td>
<td>–</td>
<td>8.465 ± 0.452</td>
<td>1.019 ± 0.054</td>
<td>–</td>
</tr>
<tr>
<td>HP94-24</td>
<td>Theog</td>
<td>1.16</td>
<td>0.05</td>
<td>1260 ± 133</td>
<td>152 ± 16</td>
<td>24.920 ± 0.450</td>
<td>2.999 ± 0.054</td>
<td>789 ± 86</td>
</tr>
<tr>
<td>UK98-1</td>
<td>Maldeota</td>
<td>8.81</td>
<td>0.60</td>
<td>710 ± 23</td>
<td>85 ± 3</td>
<td>15.373 ± 0.093</td>
<td>1.850 ± 0.011</td>
<td>587 ± 21</td>
</tr>
<tr>
<td>UK98-11</td>
<td>Maldeota</td>
<td>13.4</td>
<td>0.57</td>
<td>1225 ± 89</td>
<td>147 ± 11</td>
<td>21.384 ± 0.169</td>
<td>2.574 ± 0.020</td>
<td>638 ± 47</td>
</tr>
<tr>
<td>KU92-56</td>
<td>Maldeota</td>
<td>264</td>
<td>13.5</td>
<td>975 ± 32</td>
<td>117 ± 4</td>
<td>18.002 ± 0.134</td>
<td>2.167 ± 0.016</td>
<td>591 ± 21</td>
</tr>
<tr>
<td>KU92-58</td>
<td>Maldeota</td>
<td>18.8</td>
<td>0.79</td>
<td>1217 ± 9</td>
<td>146 ± 1</td>
<td>19.864 ± 0.139</td>
<td>2.391 ± 0.017</td>
<td>567 ± 8</td>
</tr>
<tr>
<td>UK94-58</td>
<td>Baraghata</td>
<td>–</td>
<td>0.02</td>
<td>–</td>
<td>–</td>
<td>14.263 ± 0.400</td>
<td>1.717 ± 0.048</td>
<td>–</td>
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<tr>
<td>Chert</td>
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</tr>
<tr>
<td>KU92-53</td>
<td>Maldeota</td>
<td>–</td>
<td>0.83</td>
<td>–</td>
<td>–</td>
<td>12.376 ± 0.030</td>
<td>1.490 ± 0.004</td>
<td>–</td>
</tr>
<tr>
<td>Carbonate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP94-41</td>
<td>Salapar</td>
<td>–</td>
<td>0.004</td>
<td>–</td>
<td>–</td>
<td>12.062 ± 2.343</td>
<td>1.452 ± 0.282</td>
<td>–</td>
</tr>
<tr>
<td>Leucogranite</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS-14</td>
<td>Gwaldam</td>
<td>–</td>
<td>0.004</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AL-23</td>
<td>Almora</td>
<td>–</td>
<td>0.006</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Uncorrected for blank. Os concentration in the leucogranites and carbonate could be dominated by blank.

$^b$ Calculated as $t = \frac{1}{\lambda} \ln \left[ 1 + \frac{(R_i-R)}{R} \right]$. $\lambda$ is the decay constant of $^{187}\text{Re} = 1.64 \times 10^{-11}$ yr$^{-1}$; Lindner et al. 1989). $R_0$ is the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio (assumed to be 8.5), $R_i$ and $R$ are the $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ measured in the sample. Errors are ±2σ.
characterise this boundary in the Durmala mine section based on carbon isotopes, phosphorus and other trace-metal distributions. The phosphorite band in the Durmala and Maldeota mines is sandwiched between a thin chert-black shale layer below and about a half a meter thick black shale band above (Tandon et al. 1988; Singh et al. 1998; Singh 1999). The only radiometric age reported (Sharma et al. 1992) from the Tal formation is for the chert-black shale layer underlying the phosphorite. An Rb-Sr isochron for these black shales occurring a few meters above the Krol-Tal boundary from Surkhet (near Mussoorie) yielded an age of 626 ± 4 Ma. The reliability of the Rb-Sr technique to date sedimentary deposition has been questioned in the light of distinctly different ages obtained for coarse and fine clay separates (Dickin 1995) from Yangtze gorge, China. This has led to the suggestion that the Rb-Sr ages of whole rock or coarse fraction clays primarily represent “mixed ages” of inherited and diagenetic components.

In this work, attempts have been made to determine the ages of the black shales occurring above the phosphorite band, a few meters above the Krol-Tal boundary (a few meters above the chert-black shale layer dated by Rb-Sr) using the $^{187}$Re-$^{187}$Os system. Towards this, two black shale samples (UK98-1 and UK98-11) from the Maldeota phosphorite mine just above the phosphorite band in the Tal Formation, were analysed for their Re-Os isotope systematics. They yield $^{187}$Os/$^{186}$Os of 15.373 ± 0.093 and 21.384± 0.169 respectively (table 4). Model ages for these two samples, are 587 ± 21 Ma and 638 ± 47 Ma respectively, using a value of 8.5 for the initial $^{187}$Os/$^{186}$Os ratio, the lowest value measured in the black shale sample from Almora (table 4) a location ~150 km east of the Maldeota mine. In addition, two more samples, KU92-56 and KU92-58 (table 4) from the same mine, but hand picked from the mine material, give model ages of 591 ± 21 and 567 ± 8 Ma, respectively. Implicit in this age calculation is the assumption that the initial $^{187}$Os/$^{186}$Os in black shales of the Lesser Himalaya is homogeneous over a spatial distance of a few hundred kilometers. All these four samples yield a “mean” model age of 596 ± 30 Ma. A better approach to determine the age is through isochron plot of the Re-Os data. Such an exercise for these four samples gives an age of 549 ± 32 Ma and an initial ratio of 8.98 ± 0.58 (correlation coefficient = 0.974); in agreement with the “mean” model age. The $^{187}$Re-$^{187}$Os age is consistent with that expected from stratigraphic considerations (Azami 1983; Singh and Rai 1983) and the reported ages for Pc-C boundary based on U-Pb measurements of zircons from volcanic ashes from several other locations (Bowring et al. 1993). More black shale samples are being analysed from these mines to place better constraints on their ages by the isochron method (Singh 1999; Singh et al. 1999). One outcrop sample from Theog, in the inner sedimentary belt, yields a model age of 789 ± 86 Ma (table 4). This preliminary result seems to indicate that the inner belt sediments were probably deposited a few hundreds of million years earlier than those in the outer belt. This inference, however, needs to be confirmed by more analysis.

As a part of our study to map $^{187}$Os/$^{186}$Os variations in black shales from Kumaun to Himachal Lesser Himalaya, we have analysed a few samples. The mean $^{187}$Os/$^{186}$Os and Os concentration in the samples analysed so far are ~25 and ~1 ng g$^{-1}$ (figure 2). These are significantly higher than those in the upper continental crust ~10.5 and ~0.04 ng g$^{-1}$ (Esser and Turekian 1993; Shirey and Walker 1998) respectively. These results suggest that weathering of black shales from the Lesser Himalaya could be a potential source of radiogenic Os to the rivers draining the region which in turn could contribute to the steady increase in the $^{187}$Os/$^{186}$Os in the oceans (Pegram et al. 1992; Ravizza 1993; Ehrenbrink et al. 1995; Turekian and Pegram 1997). Studies of Os concentration and $^{187}$Os/$^{186}$Os in leachable fraction of these black shales and in rivers draining them should provide a more direct assessment of their role in contributing to the Os isotope evolution.
of the oceans through time (Singh 1999; Singh et al 1999).

The analysis of two samples of leucogranite (from Almora and Gwaldam) and one Precambrian carbonate (from Himachal Pradesh), shows that Os concentrations in them are quite low (4-6 ppt; table 4), barely above process blanks. If such low concentrations are typical of leucogranites and carbonates from the region, the weathering of such rocks is unlikely to be an important source of Os to rivers draining them.

4. Conclusions

Experimental techniques for extraction and purification of subnanogram/nanogram quantities of Os and Re from environmental samples and precise determination of their isotopic composition by Negative Thermal Ionization Mass Spectrometry have been established in our laboratory following available procedures. The precision of $^{187}$Os/$^{188}$Os determination in Os loads of a few tens of picograms is $\pm 1\%$ (twice standard error of the mean). The precision of Os and Re concentration determination ($\pm 2$ s.d.) is typically 2-3%. Using these techniques, attempts are underway to date black shales from the inner and outer Lesser Himalaya and to assess their role in contributing to the Os isotope evolution of the oceans through the Cenozoic. Preliminary results show that (i) samples from the Maldeota mine are about 550-600 Ma old and (ii) $^{187}$Os/$^{188}$Os ratios in the inner and outer belt samples range from 8 to 96 (mean $\sim 25$) with Os concentrations from 0.02 to 13 ng g$^{-1}$ (mean $\sim 1$ ng g$^{-1}$). The high Os concentration and $^{187}$Os/$^{188}$Os make the black shales from this region a potential source for radiogenic Os to rivers draining them and hence to the evolution of Os isotopes in the oceans.

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