Chapter 2

Materials and Methods

A. MATERIALS

2.1 STRATIGRAPHY AND LITHOLOGY OF THE AREA

This section provides the lithological and stratigraphical framework for the study area. This thesis work is predominantly in the Lesser Himalaya and as mentioned earlier, focuses on (i) the determination of chronology of the sedimentary sequences of this region, (ii) evaluate the role of carbonates and silicates of the region in regulating the chemical and Sr isotopic compositions of rivers draining through them and (iii) assessing the importance of weathering of black shale deposits from this area in controlling the seawater $^{187}Os/^{186}Os$ evolution during the past ~25 Ma. Knowledge of the stratigraphy of the area and available data on their ages provide the base line information for chronological studies carried out in this work. For evaluating the role of these sedimentaries and silicates in determining the chemical and isotopic fluxes, emphasis will be on the lithology. Keeping these in view, efforts have been made in this chapter to summarise from the available information the origin, lithology, stratigraphy and suggested intercorrelation of the different geological units. In the north, the Lesser Himalaya is separated from the Higher Himalaya by the Main Central Thrust (MCT) while the Main Boundary Thrust (MBT) defines its southern boundary (Gansser, 1964). The Lesser Himalaya represents a relatively matured topography made of Middle Proterozoic to Early Cambrian sedimentary strata with small amount of displaced crystallines (Valdiya, 1995). The crystalline klippe divides the Lesser Himalayan sedimentaries into two NW-SE elongated sequences. The northern sedimentary sequence is known as the ***inner belt*** while the southern part, as the ***outer belt*** (Valdiya, 1980; Fig. 2.1).

(i) Outer belt sedimentary sequence

The outer belt consists of several exposed but detached synclines between Solan in Himachal Pradesh to Nainital in Uttar Pradesh. These synclines are made of thick pile of unmetamorphosed sedimentary rock sequences, which have been studied by various workers (Medlicott, 1864; Auden, 1934; Rao, 1968; Bhargava, 1972 and Shanker *et al.*, 1993) who have recognised various groups and formations in these synclines. The sedimentary successions composed of the Blaini, Infra-Krol, Krol and the Tal

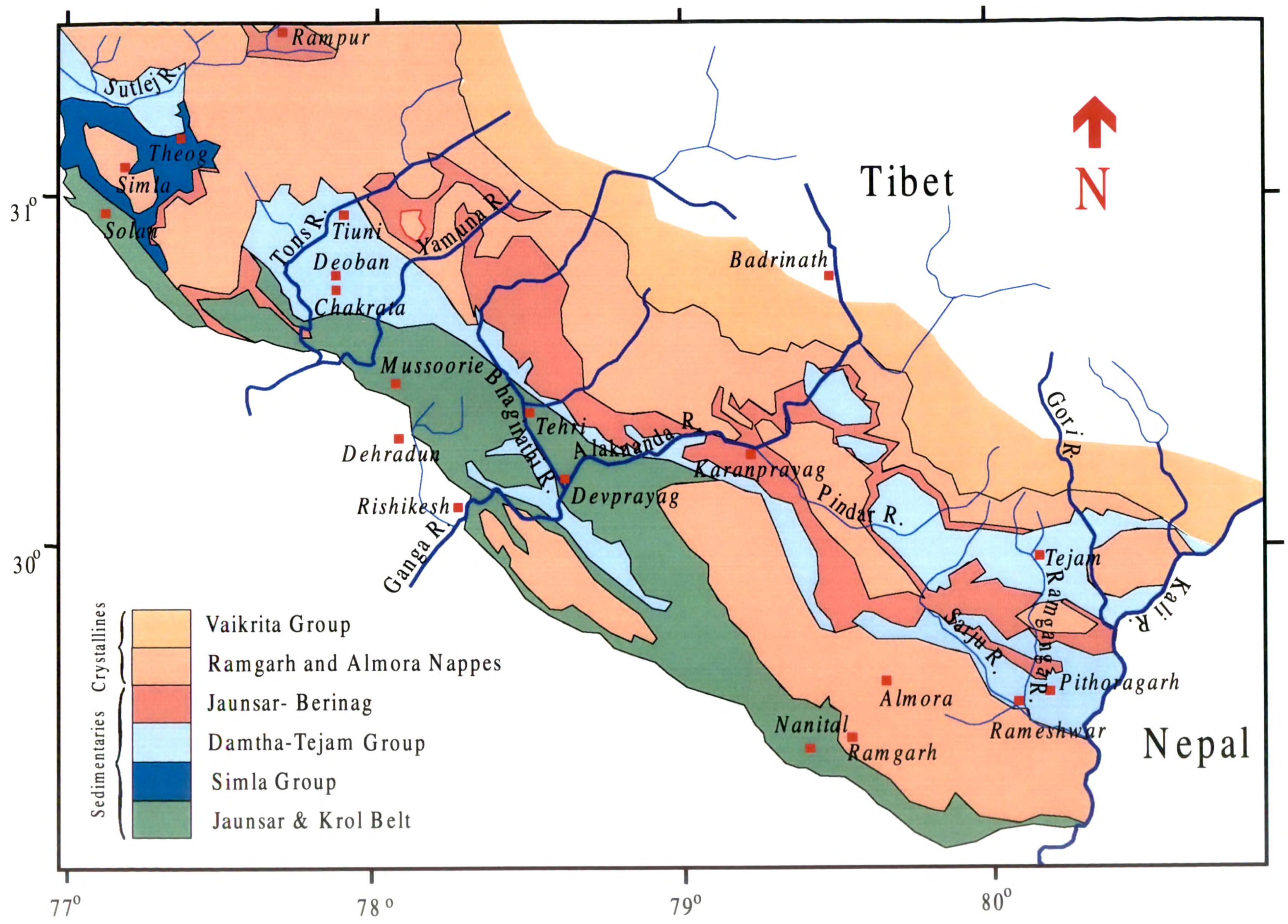


Fig. 2.1: Simplified geological map of the Lesser Himalaya.

formations together are called as ***Krol belt*** (Fig. 2.2). There are lot of controversies about their origin. Rao (1968) considered the Krol-Belt as autocthonous while Auden (1934, 1937) regarded it as an allochthon, which have been transported from the inner sedimentary belt. According to Valdiya (1995) these sedimentary sequences are para-auctothonous and they have advanced 4-21 km southward over the Siwalik zone.

The Krol belt sediments are exposed along the drainage basins of the tributaries of the Ganga, Ghaghara and the Indus rivers and their weathering may have significant influence the chemistry and isotopic composition of these rivers. In the following paragraphs brief description of the various units of the Krol belt is presented.

(a) Blaini formation

The Blaini formation, named after the river Baliana, northwest of Solan in Himachal Pradesh (Fig. 2.1), is a conglomerate with siltstones, grey, olive-green and black coloured shales and pink colour limestone. It is comprised of diamictite interbeded with quartz arenite, shale/slate and limestone. The type section is in Baliana River and the proposed reference section is on the right bank of Mussorie Syncline (Shanker *et al.*, 1993). It is represented by four horizons of diamictite. The Blaini boulder beds are composed of unsorted clast of various rock types in a structureless matrix of variable composition. Near Maldeota, clasts and matrices are dominantly dolomitic in composition and are probably derived from the underlying Shali and Deoban formations while in the Simla the Jaunsar Groups are the source of argillaceous and arenaceous clasts. This formation is inferred to have been formed in glacio-marine environment (Shanker *et al.*, 1993).

(b) Infra-Krol Formation

Infra-Krol formation overlies the Blaini formation (Fig. 2.2) and is composed of grayish black and bleached shale/slate interbedded with thin silty layers. The contact between the Infra-Krol and the Blaini formations is gradational and often difficult to demarcate. The type section for Infra Krol formation is Krol Hill, Krol Syncline near solan (Fig. 2.1). It is represented by black and bleached ash gray shale/slate. The presence of various types of bedding have led to the suggestion that these were deposited in a low energy tidal flat and lagoonal environment (Bhargava and Singh, 1980).

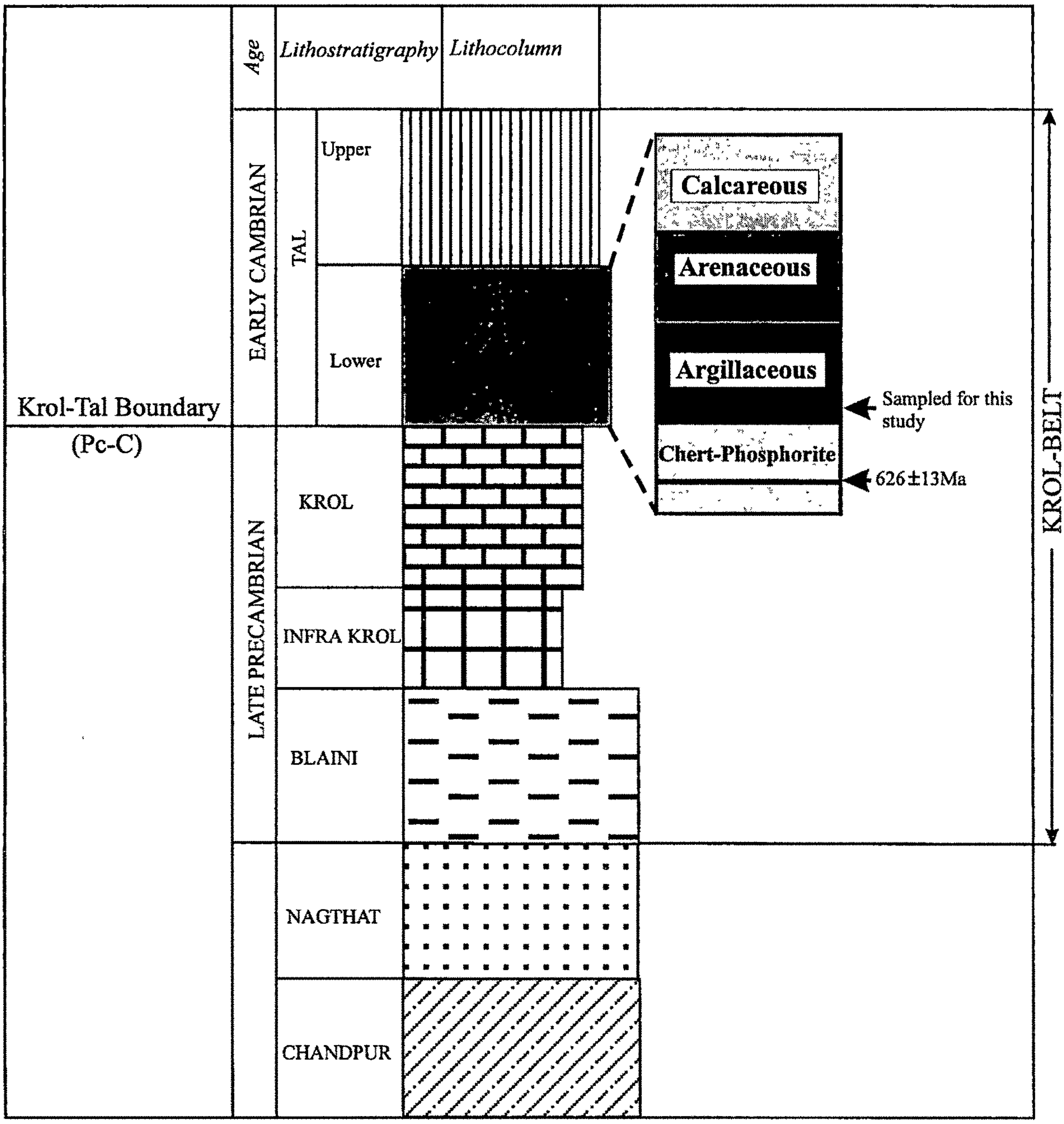


Fig. 2.2: Lithostratigraphy of the outer Lesser Himalaya. Summarised from Valdiya (1980), Tandon *et al.* (1988) and Shanker *et al.* (1993). The Rb-Sr age of black shales in the chert - phosphorite layer (Sharma *et al.*, 1992) is also given.

(c) Krol Formation

Krol formation is a thick succession of carbonate rocks with shales and sandstones. It conformably overlies the Infra-Krol formation. Valdiya (1975) and Kumar (1984) classified it into three members-Lower, Middle and Upper. The proposed type area for the Krol group is Krol Hill in Solan, H.P. and Kauriyala village in Tehri Garhwal district, Uttar Pradesh (Fig. 2.1; Shanker *et al.,* 1993). Lower Krol consists of argillaceous limestone interbedded with greenish gray calcareous shale with fine-grained calcites, some sericite and clay minerals. Middle Krol consists of purplish and greenish shale with thin lenticular limestone with or without gypsum. This member is wide spread throughout the Krol basin. The Upper Krol is represented by blue crystalline limestone and dark gray thickly bedded massive dolomitic limestone.

The Krol formation generally represents deposits of a shallow tidal sea where sediments of mostly intertidal to superatidal zone dominate (Singh *et al.,* 1978; Shanker *et. al.,* 1993). Ripple marks and other flow structures on the quartz arenite and calcareous bands of upper part of the Middle Krol member have been interpreted to represent the restoration of connection with the open sea (Shanker *et. al.*, 1993).

(d) Tal formation

This formation is composed of chert-phosphorite, areno-argillaceous and arenaceous calcareous rocks (Shanker *et al.,* 1993). It conformably overlies the Krol formation (Fig. 2.2). Mussoorie area (Mussoorie Syncline), Dehradun is proposed as reference area for the Tal formation where all its litho-units are well exposed. In this area, it is well exposed in the **Maldeota** and **Duramala** phosphorite mine sections from where black shale samples were collected for this study. It is divided into two members, the Lower and the Upper Tal.

The Lower Tal formation consists of black chert interbedded with shale and rock phosphate, ***black shale***, calcareous siltstone and siliceous limestone. The lower Tal is divided into four units, the chert-phosphorite, argillaceous, arenaceous and the calcareous units (Fig. 2.2). The chert-phosphorite unit consists of black chert interbedded with black shale and rock phosphate with occasional limestone bands. Above the chert-phosphorite band, the argillaceous layer composed of ***black shales*** (often pyritic and micaceous in nature) occur. Black shales of this layer are fine grained, consisting of muscovite, sericite, clay minerals and fine silica. The arenaceous and the calcareous units lie above the argillaceous units. The Upper Tal formation is made of quartz arenite, shale, siltstone and limestone. It conformably overlies the calcareous member of the Lower Tal formation.

The presence of chert unit has led to the suggestion of a facies change from carbonate tidal flat deposition to protected tidal flat deposition and that of rock phosphate to restricted circulation, relatively shallower water depth (Shanker, 1971). The presence of pyritiferous black shales in argillaceous member suggests euxinic environment and deoxygenated conditions (Shanker *et al.*, 1993).

(ii) Palaeontological records and ages of the various formations

Many workers have studied the fossils records of the Blaini-Infra Krol-Krol-Tal sequence. Prior to the discovery of small shelly fauna, trilobites and small brachiopods in the Lower Tal formation, this entire sequence was believed to span the time period from Permian to Jurassic (Auden, 1937). Recent discoveries of fossils (Azmi, 1983) has placed the Tal formation in the Early Cambrian (Table 2.1). Consequently, the sequences underlying the Tal group of sediments assume Neoproterozoic status. The identification of stromatolitic beds, acritarchs and filamentous-coccoidal microfossils in the Krol formation further supports this idea (Bhatt and Mathur 1990; Prasad *et al.*, 1990; Shanker *et al.*, 1993; Tewari and Azmi, 1992).

The chert-phosphorite layer of the lower Tal has been correlated with Meishucunian I of South Chinese section based on the presence of small shelly fossils and with the Tomotian Stage of Russia based on family of calcareous algae and stromatolites (Shanker *et al.*, 1993). The micro and trace fossils of the arenaceous unit of the Lower Tal formation is correlatable to Meishucunian Zone III of South China. The calcareous unit of the Lower Tal formation contains brachiopods and microgastropods, which are known from Qiongzhusian Stage of South China or the Atdabanian Stage of Siberian section.

Many workers have attempted to precisely date the sedimentary rocks from the close vicinity of Pc-C boundary of known stratotype sections, with a view to assign "age" for the Pc-C boundary. The Rb-Sr ages of black shales collected just above the boundary from the South Chinese section range from 569 to 602 Ma (Xue, 1984; Zhang *et al.*,

Table 2.1: Various stromatolites/fossils findings and probable ages of various formations

Formation	Fossils/Stromatolites	Assigned ages/period	Ref.
Tal	conodonts and other small shelly fossils, trace fossils, small brachipods, gastropods	Early Cambriam	Azami *et al.*, 1981; Azmi 1983; Singh & Rai 1983; Bhatt *et al.*, 1985; Brasier & Singh, 1987
Krol	Several forms of stromatolites, Ediacaran fossils	Late Proterozoic to Vendian	Singh & Rai, 1977; Shanker *et al.*, 1993; Shanker & Mathur, 1992,
Blaini/Infra -Krol	Acritarchs, cyanobacterial filaments, coccoids	Late Proterozoic	Prasad *et al.*, 1990; Tewari & Azmi, 1992
Mandhali	Stromatolites e.g. *Jurusania, Collenia parva*	Upper Riphean	Valdiya, 1980
Deoban	Stromatolites e.g. *Baicalica baicalia, Masloviella Columnaris*	Middle Riphean	Valdiya, 1980

1984). Similarly, Sharma *et al.,* (1992) have dated black shales from the chert-phosphorite unit of the Lower Tal by Rb-Sr and obtained an age of 626±13 Ma. These Rb-Sr ages are a few million years older compared to U-Pb ages, 520-545 Ma, obtained on the zircon separates from the volcanic ash interlayered between sedimentary rocks near the Pc-C boundary of Canada, Morocco, China, Siberia and South Australia (Bowring *et al.,* 1993; Brasier *et al.,* 1994). Based on these U-Pb ages, the Pc-C boundary has been assigned an age of ~545 Ma (Brasier *et al.,* 1994). The only radiometric age available for the Krol belt section from the Lesser Himalaya, as mentioned earlier, is that based on Rb-Sr for the black shales of chert-phosphorite unit of the Lower Tal formation (Sharma *et al.,* 1992). Ahron *et al.* (1987) and Banerjee *et al.*(1997) have characterised the Krol-Tal boundary (Pc-C boundary) in this section based on carbon and oxygen isotopes and trace element studies of Krol carbonates and Tal phosphorites.

One of the goals of this study is to explore the possibilty of dating the black shales from the Lower Tal section using the Re-Os chronometer and thereby provide an "age" for the Pc-C boundary. With this view, as well be discussed later, black shales samples from these sections have been collected and analysed for Re, Os isotopes systematics and their composition.

Another objective of this thesis is to assess the role of weathering of carbonates and silicates in regulating the chemical and Sr isotope compositions of the rivers flowing through the southern slops of the Himalaya. In this context, the lithologies of the different formations are important which were briefly described earlier. Many of these formations are exposed in the drainage basins of the Tons, the Yamuna, the Ganga and the Kali rivers (Fig. 2.1). The extensive carbonate outcrops of the Krol formation is of particular interest as it has been shown that major ion chemistry of the rivers is dominated by the weathering of carbonates. In this study the contribution of the Lesser Himalayan carbonates to the Sr abundance and $^{87}Sr/^{86}Sr$ of the rivers will be evaluated. The presence of evaporites along with the carbonates are reported in the Krol formation (Shanker *et al.*, 1993). They may also be important in contributing to the Sr isotope systematic of the Ganga headwaters. In view of this, several carbonate samples have been collected from the Krol formation exposed in Solan (H.P.) to Nainital (U.P.) in the outer belt; for their chemical and isotope composition, these are discussed in the later sections.

The presence of black shales in the Tal, Blaini-InfraKrol and Krol formations has been discussed earlier and form important exposures of black shales in the Lesser Himalaya. Many of these have been sampled during this study (see section 2.1) to determine their chronology (and hence that of Pc-C boundary) and to assess their potential in contributing to the Os isotope evolution of the oceans. It is suggested (Pegram *et al.*, 1992, Ehrenbrink *et al.*, 1995; Turekian and Pegram, 1997) that weathering of black shales from the Himalaya may have caused the steady increase in the Os isotopic composition of the oceans through the past few tens of Ma. As these black shales are quite old, the Os isotopic ratios in them could be very high, weathering of which can supply highly radiogenic Os to the rivers and finally to the oceans.

(ii) Inner belt sedimentary sequence

The inner belt sedimentary sequence of the Lesser Himalaya lies to the north of the outer belt towards MCT. It is a tightly folded repeatedly faulted auctothonous sedimentary pile (Valdiya, 1995). The autocthonous unit of the inner belt is divided into two groups, ***Damtha and Tejam*** (Fig. 2.3). The Damtha is conformably succeeded by the ***Tejam group***, comprising of Deoban (≈Shali) and Mandhali (Sor) formations (Fig. 2.3). The Deoban is made predominantly of dolomites and contain in them branching stromatolites (Valdiya, 1980). This formation grades upwards into the pyritous-carbonaceous slates, marls and interbeded calcitic marbles of the Mandhali formation. As the Deoban (≈Shali) and Mandhali are made of huge carbonate deposites, they are of interest to this work in assessing the role of carbonates in contributing chemical constituents and Sr to the rivers flowing through them. Many of the rivers such as the Beas, Sutlej, Alaknanda, Pindar, Ramganga, Sarju and the Kali all flow through the Deoban (≈Shali) and Mandhali carbonate deposits. Carbonates from these areas have undergone low degree of metamorphism.

Occurrences of black shales have been reported in the Deban and Mandhali formations (Rupke, 1974; Valdiya, 1980). These black shales also have been sampled in this study (see section 2.1) for determining their chronology and use the data for stratigraphic inter-correlation with outer belt black shale deposits.

In veiw of the above, these two formations have been discussed in some detail below.

(a) Deoban formation

The Deoban formation consists of stromatolite bearing, cherty dolomite and dolomitic limestone with bands and intercalations of blue limestone and grey slate (Valdiya, 1980). There are two facies of the Deoban lithology, one is developed in southeast of the Alaknanda river in the Gangolihat area of Pithoragarh district and other that is recognizable in the Deoban mountain in the Chakrata area (Fig. 2.1). The first one falls in the drainage area of the Alaknanda, Pindar (headwaters of Ganga) and Sarju, Ramganga, Kali (headwaters of Ghaghara) rivers while the later one forms a part of the drainage basins of the Yamuna and the Tons rivers. Shali formation in the Himachal Pradesh is equivalent to the Deoban formation (Valdiya, 1995) and it forms a part of the

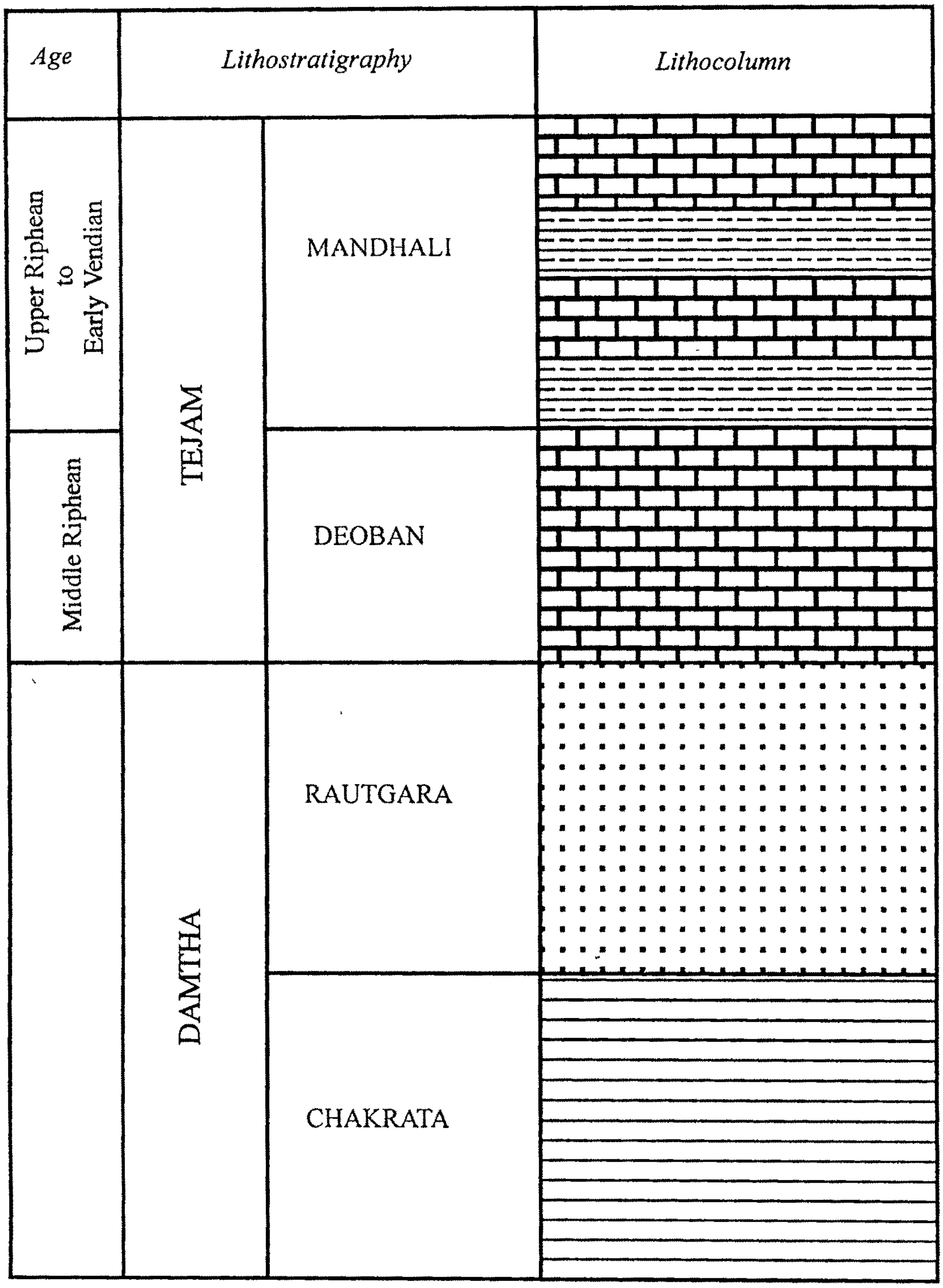


Fig.2.3: Lithostratigraphy of the inner Lesser Himalaya. Summarised from Valdiya (1980)

drainage basin of the Sutlej river. In the Thal-Tejam-Girgaon area these limestones are metamorphosed and the degree of metamorphism increases towards the MCT (Bhattacharya, 1982). In the Baram area these are in contact with Toli gneisses. Based on the sedimentary structures and associated stromatolites Kumar and Tewari (1978) suggested an inter-tidal to a carbonate tidal flat deposition for these carbonates. The occurrence of oolites in these deposits has led to the suggestion of a shallow, warm and agitating marine environment for their deposition.

(b) Mandhali formation

Mandhali succeeds the Deoban discordantly in the Chakrata area, but with break or unconformity elsewhere. It consists of greyish green and black carbonaceous pyritc phyllites or slates interbedded with blue limestones and a vareity of conglomerate made of clasts. In the Gori (tributary of Kali) valley it contains pyritous slates massive dolomite limestone with chert laminae. In this area limestones are intruded by dolerite which have given rise to marble in contact zones. In the Thal-Tejam area (Ramganga valley) it is represented by pyritous carbonaceous phyllites interbebed with limestone. According to Valdiya (1980), the presence of carbonaceous substances in them denotes poorly ventilated euxinic environment for their deposition. The conglomeratic horizons within the succession indicate intervals of disquiet and interrupted sedimentation in an unstable shelf-environment.

2.1 (iii) Intercorrelation between Inner and outer belt sedimentaries

Intercorrelation between the inner and outer sedimentary sequences is a difficult task due to the lack of sufficient fossil records and radiometric ages. Many workers have tried to correlate these two sequence based on lithology and more recently based on the available few fossil records.

West (1939) has correlated the Deoban (=Shali) formation of the inner belt with the Krol of the outer belt and Rautgara (inner) with Blaini (outer) based on lithology (Fig. 2.4). Frank and Fuchs (1970) and Valdiya (1995) have followed the same convention.

But other workers (Mehr, 1977; Stocklin, 1980; Shanker *et al.,* 1993) suggest that the Krol belt of the outer belt is much younger than the Tejam group of rocks (Fig. 2.5)

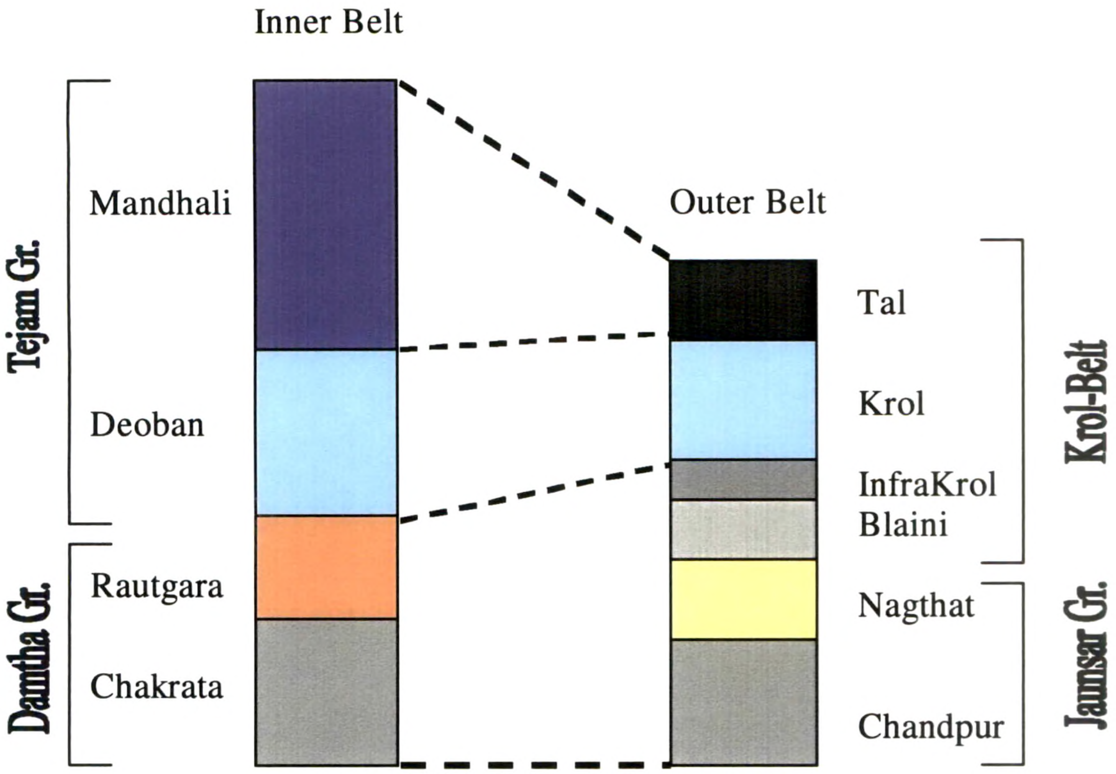


Fig. 2.4:The inter-correlation between inner and outer sedimentary sequences as suggested by West (1939) and Valdiya (1995).

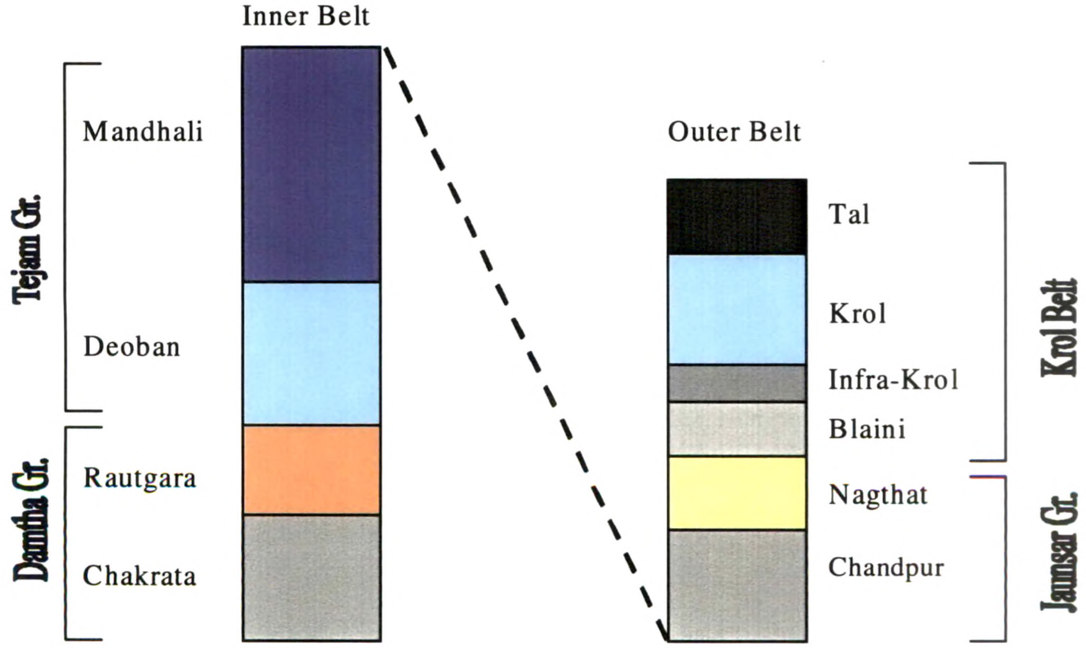


Fig. 2.5: The correlation between the inner and outer belt as suggested by Mehr (1977); Stocklin (1980) and Shanker *et al.* (1993). In model the Mandhali of inner belt lies below the Chandpur formation of the Jaunsar group.

and that the Mandhali formation is the base of the Jaunsar group (Chandpur and Nagthat formation) on which the Krol belt is overlying.

Recently, Sharma (1998) proposed that the inner and outer belt sediments deposited in the same basin and due to tectonic activity sometime in Precambrian, sea regressed southward in the Lesser Himalaya resulting in the cessation of sedimentation in the inner belt and continued in the outer belt. As a result, there is no sedimentary rocks present above the Mandhali formation in the inner belt. He supports the model in which Mandhali is considered as the base of Chandpur (Fig. 2.5).

It should be possible to check on the stratigraphic correlation between the inner and outer belt sediments and thereby check the validity of the above models, if their chronology can be ascertained. The attempt in this thesis to date black shales from the inner and outer belt is a step in this direction.

As discussed earlier a part of the work in this thesis deals with the weathering of the different lithologies and their contribution to the chemical and isotopic composition of the headwaters of the Ganga, Ghaghara and Indus. In the following (Table 2.2) the broad lithology of the drainage basins of different river system has been summarised.

Table 2.2: Lithology of drainage basins of major rivers of the G-G-I source waters

Ganga System	
Bhagirathi	Originates in the Higher Himalaya and flows through the Crystallines before entering the Lesser Himalaya, where it drains metasediments (quartzites and dolomitic limestones) and metabasics.
Bhilangna	It flows mostly through the Higher and Lesser Himalayan Crystallines. Near its confluence with the Bhagirathi it drains Nagthat quartzites, phyllites, greywackes and limestones.
Alaknanda	In the Higher Himalaya, it originates and drains the Higher Himalayan Crystallines. In the Lesser Himalaya it flows through carbonates of Deoban and Mandhali, massive quartzites and slates, phyllites and greywackes of Nagthat formation.

Ganga	Ganga takes its name at Devprayag after the confluence of the Bhagirathi and the Alaknanda. Downstream of Devprayag it passes through Nagthat quartzites, Krol limestones, phyllites of InfraKrol, the Siwaliks and alluvium in the plains.
Ghaghara	
Sarju	At its origin, Sarju passes through the Higher Himalayan Crystallines. It flows towards south west, predominantly through famous Calc Zone of Tejam carbonates, slates and quartzites of Rautgara before joining Ramganga.
Ramganga	Ramganga drains relatively larger stretch of Higher Himalayan Crystallines in its upper reaches. Downstream, it flows through lithologies similar to those described for the Sarju and in addition through a band of Lesser Himalayan Crystallines (Askot Klippe).
Kali	The river Kali drains a number of lithologies. In its upper reaches it flows through the Higher Himalayan Crystallines, and downstream it drains carbonates and slates of Deoban and Mandhali formation, quartzites and phyllites of Rautgara formation, the Lesser Himalayan Crystallines (Almora Nappe), and the Siwaliks.
Indus System	
Sutlej	Originates near Mansarovar Lake and flows through the crystallines, gneisses, granites, phyllites, schists, carbonates and quartzites. Further downstream, it drains the carbonates of Shali Fomation.
Beas	It originates near Rohtang Pass (Higher Himalaya), flows through the crystallines, carbonates and Tethys sediments

B. METHODS

The objectives of this thesis, as mentioned in the earlier chapter, are to (i) determine the chronology of black shales from the Lesser Himalaya, (ii) assess the role of weathering of these black shales in controlling the $^{187}Os/^{186}Os$ of seawater and (iii) evaluate the impact of weathering of carbonates and silicates in governing the chemical and Sr isotopic composition of the Himalayan rivers.

To achieve these goals, it is necessary to collect suitable samples and analyse them for their mineralogy, petrology (microscopic studies), chemical and isotopic composition. Sample characterisation has been done based on the microscopic studies of their thin sections and using x-ray diffraction. Chemical analyses of the samples have been carried out using a variety of analytical techniques such as Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Atomic Absorption Spectrometry, UV-Visible spectrophotometry, Ion chromatography, CN analyser and coulometer. For isotopic analysis Negative Thermal Ionisation Mass Spectrometry (N-TIMS), Thermal Ionisation Mass Spectrometry (TIMS) and Stable Mass Spectrometry techniques were used. These are discussed in some detail below.

2.2 FIELD SAMPLING

Sampling is a critical component of this work and considerable efforts were put in for their collection. The samples analysed in this study were collected in five field campaigns conducted during 1992, 1994, 1995, 1996 and the last in 1998. I had participated in the campaigns of 1994, 1996 and 1998, the samples from the other campaigns were made available to me for this work.

(i) Black shales

Black shale samples were collected from the various geological formations and locations in the Lesser Himalaya. For chronological work, black shale samples were collected from the two underground phosphorite mines, Maldeota and Durmala near Mussoorie These sites were chosen, as sufficient lithological and stratigraphical information were available from these areas (see section 2.1). In addition, the Rb-Sr age for the Lower Tal formation provided an idea of the chronology of these formations. Also sampling from underground mines is likely to minimise weathering and mobilisation effects. These samples were collected from the argillaceous unit of the Lower Tal formation (Fig. 2.2) in both the mines which is ~10 m above the Krol-Tal (Pc-C) boundary.

The samples UK98-1 to UK98-11 were collected from the Maldeota phosphorite mine at three altitudes in strike direction of the bed, from a stretch of ~1 km. Two more samples KU92-56 and 58 are also from the same mine but were picked from the pile of black shales kept outside the mine during phosphorite mining. They also belong to the same argillaceous unit of the Lower Tal (Fig. 2.2).

The UK98-17 to 31 were sampled from the Durmala mine. These samples were collected from the two limbs of the anticlinal bed of argillaceous unit separated by ~3 km. UK98-17, 18 and 19 were from one end whereas UK98-28 and 31 from others.

All these black shale samples, in hand specimen, were black, hard and compact with presence of thin laminations. Fresh shining pyrites were present in almost all of them. In some samples pyrites were distributed through out the matrix whereas some of them contained larger size (few millimeter to centimeter) pyrite concretions. It can be inferred from the presence of these shining pyrites that effects of weathering in these samples is unlikely to be significant.

For the chronology of the inner belt sediments of the Lesser Himalaya, samples were collected from the Shali formation in Theog. These samples are from road cut exposures and were collected a few centimeters below their exposed surfaces. HP94-22 to 26 were sampled from this region.

To evaluate the impact of weathering of black shales from the Lesser Himalaya on the seawater Os isotopic composition, a reconnaissance study of the Os isotopic composition has been done in which samples from several drainage basins of the major headwaters of Ganga-Ghaghara-Indus river system were analysed. The samples for this purpose come mainly from surface exposures of four localities, Nainital, Almora, Mussoorie and Simla (Fig. 2.1). The Nainital samples (KU92-49 to 51) belong to the Upper Krol formation, the Almora samples (KU92-2 and 6) are from Almora crystallines and are basically black graphite schist. These exposures form a part of the drainage basins of the headwaters of the Ganga and Ghaghara syatems. KU92-53, 57, UK94-51 to 66 were sampled from the road cut exposures of different localities of the Mussoorie hills. They are from Upper Krol and the Lower Tal formations. This area falls in the drainage basin of the Ganga River system.

As discussed above inner belt samples were collected from the Shali formation at Theog near Simla (Fig. 2.1).

(ii) Carbonates

To determine the influence of the Lesser Himalayan carbonates on the chemical and Sr isotopic composition of the headwaters of G-G-I, a detailed sampling of these carbonates have been done covering a wide geographical area from Bilaspur in Himachal Pradesh to Pithoragarh (near Nepal border) in Uttar Pradesh,. Samples collected for this study are from almost all the carbonate bearing formations of the inner and outer Lesser Himalaya, discussed in section 2.1. The samples from the inner belt are from Deoban and Mandhali formations of the Tejam group and Shali formation (equivalent of Deoban in Himachal Pradesh) whereas the outer belt samples primarily belong to the different units of the Krol formation and one from Blaini formation. These formations are sampled from the road cuts or the natural exposures.

The samples KU92-9, 13, 22, 26, 36, 43, 46 and UK95-12, 19 were collected from the Deoban and Mandhali formations in the Gangolihat- Pithoragarh and Thal-Tejam-Pipalkoti area of the inner Lesser Himalaya. The sample KU92-26 is from the northern Tejam region, where these units have gone through a low degree of metamorphism due to the proximity of Main Central Thrust (Bhattacharya, 1982). The samples KU92-13, 43 and UK95-19 are from regions near Gangolihat where evidence of carbonate diagenetic processes of dolomitization and silicification have been reported (Kumar and Tewari, 1978). The sample KU92-22 is from the southern part, and KU92-36 and UK95-12 are from northern part of the Thal-Tejam exposure. The sample KU92-36 was in contact with augen gneisses. UK95-12 is from Pipalkoti, where massive deposits of rhythmites are exposed. The sample KU92-46 is collected at the contact of carbonate and slate. All the above samples are part of the drainage basins of Ghaghara system except UK95-12, which is a part of the Alaknanda basin (Ganga system) (Fig. 2.1).

The samples HP94-41, 42 and 43 are from the Shali formation a part of the drainage basin of Sutlej. These samples are generally intercalated with slates.

The samples UK94-76, 77, 78 and 97 are from the Deoban formation exposed in Chakrata-Deoban-Tiuni area. These are a part of the drainage basins of the Tons and Yamuna rivers (Fig. 2.1).

The sample VBL-1 is from the Blaini formation. Other samples are all from Krol formation collected from the Mussoorie hills except HP94-13 which comes from the Krol formation of Solan (HP) area (Fig. 2.1).

(iii) Water samples

Water samples were collected from the Ganga, Alaknanda, Pindar, Sarju, Ramganga and the Kali rivers during the field campaign of 1996 for major ion chemistry. The samples were collected in pre-cleaned plastic bottles as far away as possible from the river bank. After collection, one aliquot of the water (~250 ml) was filtered at site through 0.45 µm nucleopore filter contained in an acrylic set-up (Sarin *et al.*, 1992). Two other aliquots one ~500 ml and the other ~1000 ml were also collected and brought to laboratory as such for analysis.

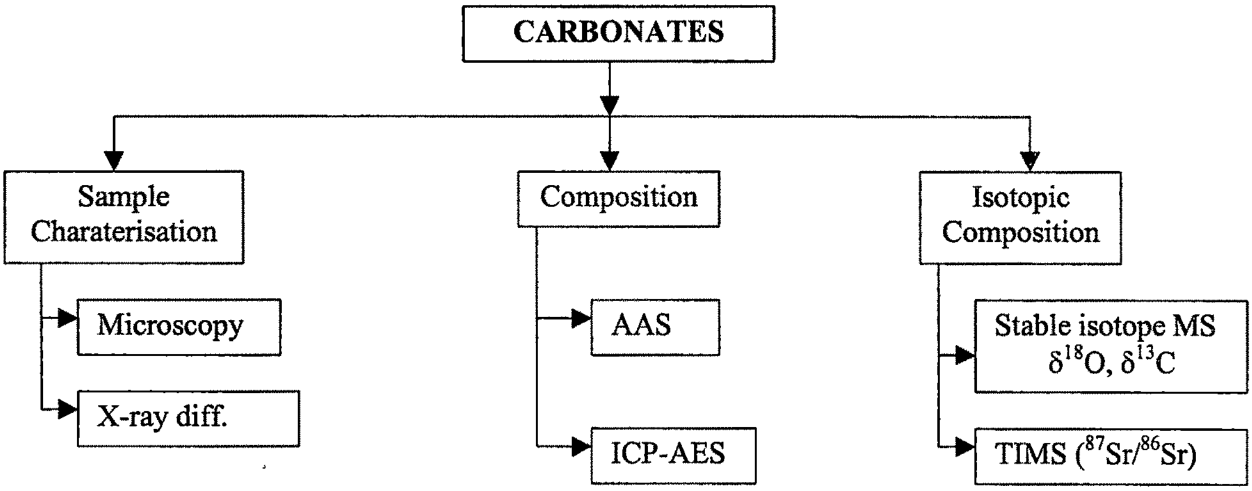
2.3 POWDERING

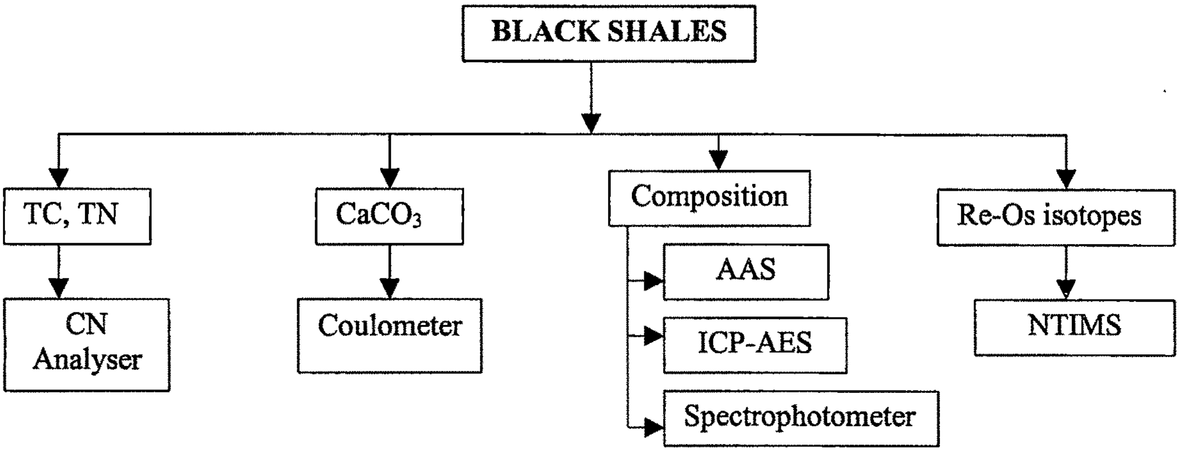
In the laboratory, the carbonate and black shale samples were powdered from the field samples. Towards this, the field samples were broken to chips of mm to sub mm size using agate mortar and pestle. From these chips about 250 grams of samples were finely powdered using agate Tema mill and stored in cleaned plastic containers. In last phase of the work, the final powdering was done with SPEX mill using an acrylic container and methylcrylate balls. These powders were sieved using 100 µm nylon sieves, the >100 µm fraction was repeatedly powdered to ensure that the entire sample is brought to <100 µm. Care was taken to avoid any contact with metals and metal surfaces during this entire operation. Typically an amount of about 40-60 grams of samples were powdered using the SPEX mill. These powders were used for various chemical, isotopic and XRD analyses.

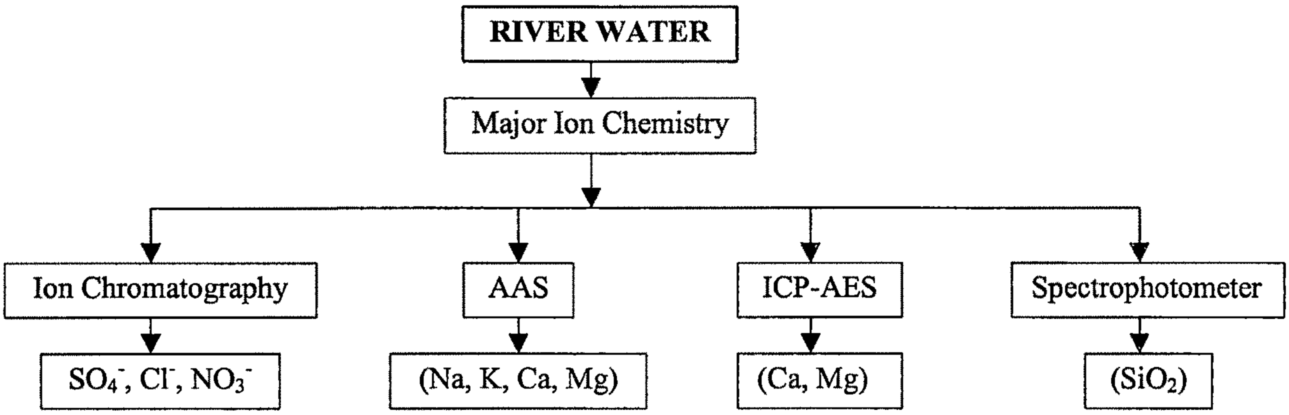
2.4 ANALYTICAL TECHNIQUES

The analytical techniques were employed depending on the type of the samples and the information sought from them. Of all the analytical techniques employed in this study, considerable efforts and time was spent in establishing the chemical procedures for the extraction and purification of Re and Os from black shales and their isotopic analysis by negative thermal ionisation mass spectrometry (Trivedi *et al.*, 1999). These procedures, established for the first time in our laboratory (and in India) are based on

ANALYTICAL SCHEMES FOR THE SAMPLES







those available in literature. The chemical procedure and measurement technique have been described in detail in this section, whereas other analytical methods are briefly presented as they are routinely used in our laboratory.

(i) Re-Os isotope measurement 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 (Table 2.3; Esser and Turekian, 1993; Ravizza and Turekian, 1991; Shirey and Walker, 1998).

Table 2.3: Re, Os abundances and $^{187}Os/^{186}Os$ in some geological and environmental samples

Samples	Re (ng g^{-1})	Os (ng g^{-1})	$^{187}Os/^{186}Os$
<u>*Meteorites*</u>			
Chondrite	42 - 97	417 - 1050	~1
Iron	0.78 - 4820	8.8 - 65,740	~1
<u>*Mantle*</u>			
MORB	0.5 -2	0.001 - 0.05	~1
OIB	0.1 - 1	0.01 - 0.5	~1
Average continental crust	<1	<0.05	10 - 15
Granitoids	0.076 - 0.125	0.004 - 0.007	13 - 31
Mn Nodules		0.25 - 2.39	5.13 - 10.96
Black sea sediments	21 - 184	0.23 - 0.69	5.71 - 7.44
Pelagic sediments	0.076 - 1.49	0.135	6.0 - 6.7
Black Shales	30 - 1000	0.36 - 7.4	24.3 - 70.3

The 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. Low concentrations of Re and Os in the materials analysed in this study also requires the chemical and procedural blanks to be as low as possible. In this work these have been achieved using high purity chemicals.

(a) Re, Os standards, Spikes and Reagents

The Re and Os standards and spike solutions, used for the calibration and standardisation of mass spectrometric procedures and the determination of Re and Os concentrations were obtained from G. Ravizza (WHOI) and W. Pegram (Yale University). The Os standard solution is a spec pure solution of $(NH_4)_2OsCl_6$ in 6N HCl and had a concentration of 411 µg Os g^{-1} solution (Esser, 1991). The Os spike solution is enriched in ^{190}Os with an isotopic composition of 96.6% ^{190}Os, 1.9% ^{192}Os, 1.0% ^{189}Os, 0.5% ^{188}Os and < 0.1% ^{187}Os, and a concentration of 13.720±0.129 µg g^{-1} solution (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% ^{185}Re (Ravizza, 1991). These standards and spikes were suitably diluted for our use using appropriate high purity acids and were recalibrated to ascertain their strengths. The recalibration results are as follows:

Os Standard and Spike

The Os standard of 411 µg g^{-1} was diluted with high purity 6N HCl to yield a strength of 7.802 ng g^{-1}. The spike was diluted to yield two working solutions with the concentrations of 19.23 ng g^{-1} (OS2) and 0.74 ng g^{-1} (OS3). All the diluted standards and spikes were kept in pre-cleaned fluon bottles fitted with Teflon dropper. The diluted standard was calibrated with OS2 thrice. The repeats are

(i)	7.89 ng g^{-1}	(10.12.1997)
(ii)	8.04 ng g^{-1}	(12.12.1997)
(iii)	7.92 ng g^{-1}	(20.01.1998)

Mean 7.95 ± 0.08 ng g^{-1}

This is consistent with the expected value of 7.80 ng g^{-1} from the dilution.

Re Standards and Spikes

Similar to Os standard and spike, Re standard and spike solutions were also acquired from Yale University. The Re standard has a strength of 118.3 µg g^{-1}. This was diluted in high purity 1N HNO_3 to yield strength of 37.6 ng g^{-1}. This standard was calibrated using a spike obtained from Dr. G. Ravizza, WHOI with a strength of 1.568 ng g^{-1}. Repeat measurements yield for the concentration in standard solution values of

37.48 ± 0.02 ng g^{-1}
36.60 ± 0.09 ng g^{-1}
37.15 ± 0.08 ng g^{-1}
37.50 ± 0.07 ng g^{-1}

Mean 37.22 ± 0.03 ng g^{-1}

This is consistent with the expected value of 37.6 ng g^{-1} based on dilution. Using this standard, another Re spike (from Yale) was calibrated. The strength of the spike is 65.88 ± 0.07 ng g^{-1}. This was labelled as SPIKE 1C and used for our work.

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, H_2SO_4, HNO_3 and HBr were procured from SeaStar Chemicals Inc., Canada; HCl was purified in the laboratory by distilling analytical grade acid at sub-boiling temperatures first using a quartz still and then redistilled with a Teflon distillation set-up (Mattinson, 1969). Ni powder was obtained from Aldrich Inc. (99.999% purity; mesh size 100). The reagents for fusion, Na_2CO_3, $Na_2B_4O_7$ $10H_2O$; and S were all of analytical grade quality. H_2O_2 is analytical grade from Qualigens, Bombay. Commercially available distilled water was first purified using Milli-Q system and redistilled twice at sub boiling temperatures in quartz (QD H_2O) for wet chemistry.

All glasswares used were first cleaned in Milli-Q water, then boiled in hot conc. HNO_3, rinsed profusely in Milli-Q water and finally with QD H_2O. The Teflon wares used were procured mainly from Savillex Corporation, USA. They were first cleaned in milli-Q water, then in hot conc. HNO_3 for 3-4 days. They were then filled with a cleaning solution containing HNO_3, HF and H_2O in 2:2:1 ratio, sealed, wrapped in transparent cling films and kept under infra red lamp for several hours to days. The acid is emptied, rinsed several times with Milli-Q water and then with QD H_2O prior to use.

(b) Os Chemistry

Sample Decomposition Technique

The Os from various geological samples (black shales, igneous rocks, river and sea sediments) was extracted by NiS fusion and purified by distillation and ion exchange methods (Fig. 2.6; Luck and Allegre, 1983; Esser, 1991; Pegram *et al.*, 1992). Typically, 0.5 - 2.0 gm of samples were used for the analysis. The samples were first mixed with the fusion flux ($Na_2B_4O_7$ $10H_2O$, Na_2CO_3) in the ratio 1:2 and the Borax to sodium carbonate ratio is 2:1, and then with Ni (~250 mg) and S (~175mg) using a small agate mortar and pestle. After homogenising the sample and fusion mixture about half of it is placed in a "Coors" porcelain crucible (acquired from Thomas Scientific, USA) and made a crater at its centre. To this, a known weight of Os spike solution was added, and covered with the rest of the sample mixture. The small crucible containing the sample fusion flux mixture was kept in a bigger crucible, covered with lid and placed in a muffle furnace at 800°C. The temperature was raised to ~1080°C and kept at this temperature for 2 - 3 hrs. The furnace was switched off ,the melt allowed to cool in the furnace and crucible was broken to remove the NiS bead. Usually one large NiS bead was recovered, sometimes one large and many smaller beads were also found. The beads were usually smooth with metallic lustre and free from any adhering glass. The NiS bead was weighed to determine yield, which generally was in the range of 70%-90%. The bead was dissolved by refluxing it for several hours with distilled 6N HCl in a conical flask covered with a Teflon lid at sub-boiling temperature. The NiS bead generally dissolved in about 6-8 hours. The solution was cooled to room temperature, filtered through 25 mm dia 0.45 μm Millipore filter set up to separate the insoluble sulfides which are known to retain Os quantitatively. The filter paper was carefully removed, folded and placed in a precleaned 250 ml distillation flask.

Distillation

This step is necessary to separate Os from less volatile (Re) and non volatile elements whose molecular and atomic species interfere during Os mass spectrometry, e.g. ^{187}Re with ^{187}Os. This process takes the advantage of high volatility of Os as OsO_4 at 104°C. About 10 ml conc. H_2SO_4 was added to dissolve the filter paper and then ~80 ml QD H_2O to make the acid strength ~4N (water was added slowly to minimise heating) so

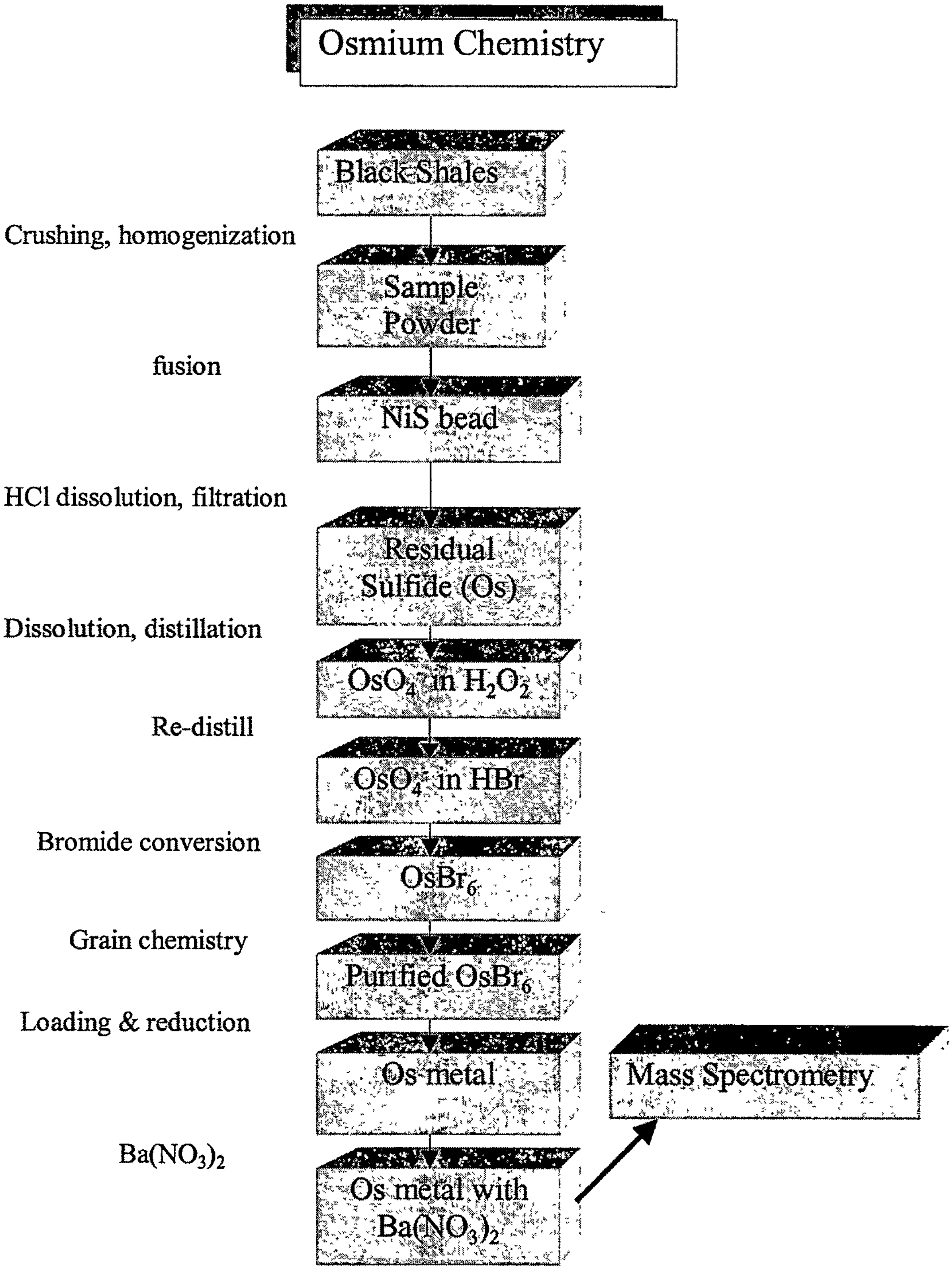


Fig. 2.6: Flow diagram for Os chemistry

that boiling point of the solution will be ~105°C. To this ~3 ml of 4N H_2SO_4 containing ~300 mg CrO_3 was added as oxidant. The 250 ml round bottom flask containing the solution was connected to a condenser system. The outlet tube of the condenser was dipped into a test tube containing 8 ml H_2O_2. The H_2O_2 trap was kept cool with ice. All the joints were sealed with Teflon tape. Both condensers were cooled with running tap water. The mixture was distilled using purified air as carrier gas following the procedure outlined by Luck (1982) and modified at Yale (Martin, 1990). The solution was brought slowly to boiling. When the solution started boiling the water in the reflux condenser was turned off and the Os distillate was collected in the ice cooled H_2O_2.

The Os distillate in H_2O_2 was further purified by distilling it into ~8ml HBr by second distillation. For this, the H_2O_2 distillate was transferred to a 125 ml round bottom flask and Os was distilled into 8 ml HBr (Esser, 1991).

Conversion to Osmium hexa bromide and grain chemistry

The HBr containing the Os was transferred to 15 ml Savillex digestion well, sealed and kept at 80°-100°C overnight in an oven. The solution was then slowly evaporated to 0.5 ml on a hot plate, transferred to the cap of the digestion vessel and taken to near dryness (~1μl). This was diluted to 10 μl with QD H_2O to make the acid strength 1N. One grain of precleaned Chelex-20 (20-50 mesh) ion exchange resin is picked and placed in a 5 ml Savillex vial. It is cleaned with conc. HBr and conditioned with 1 N HBr by ultrasonicating. To this, the 10 μl sample solution was loaded, ultrasonicated for 45 minutes and the solution was pipetted off using a microsyringe. The resin bead was washed with 10 μl of 1N HBr, ultrasonicated for three minutes and the solution was pipetted off. This step was repeated thrice. The Os from bead was eluted with Conc. HBr. Towards this, 10 μl of conc. HBr was put on the bead and ultrasonicated for 45 minutes. This HBr fraction was carefully collected as it contains Os. This step was repeated to ensure quantitative retrieval of Os.

Loading and Metal conversion

The purified Os was slowly evaporated to <1μl and carefully loaded onto Os-Re free, Pt filament (H. Cross Company, USA) using a Teflon capillary coupled 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. The Os fraction after loading on the degassed Pt filament was dried at ~0.5 amp. current. It was then heated to dull red heat (~600°C) under vacuum ($<10^{-7}$ torr) for 8-10 hours to reduce it to Os. Now this is ready for isotope measurements using NTIMS.

(c) Re Chemistry

For the determination of Re concentration, in the earlier phase of measurements, samples were brought into solution by acid digestion and Re purified by ion exchange procedure (Ravizza, 1991; Shen *et al.,* 1996), later the procedure was modified slightly and samples were ashed at 450°C prior to acid dissolution (Fig. 2.7).

Acid dissolution

About 0.25 g of powdered samples were taken in 15/30 ml Savillex digestion vessels, wetted with QD H_2O and a few drops of conc. HNO_3. To this, Re spike was added followed by ~10 ml conc. HNO_3. The vessel was sealed and kept at 80°-100°C on a hot plate for ~24 hours after which it was opened and placed on a hot plate to evaporate the HNO_3. The residue was digested twice, each time with ~ 5 ml HF, taken to dryness first with HNO_3 and then with aqua-regia to bring it to solution. In some samples, particularly in black shales from the Himalaya, there was often a small amount of dark residue; even after repeated HNO_3 and aqua-regia treatments which interfered with the Re chemistry and mass spectrometry. Therefore, the samples were ashed to oxidise the organic carbon before dissolution.

Ashing and Acid Dissolution

To avoid interference of organic matter with the Re chemistry the black shale samples were first ashed at 450°C for ~12 hrs. (Colodner *et al.,* 1993). The ashed samples were later brought to solution by acid digestion. The sample solution is brought to dryness and taken in about 7 ml 0.8N HNO_3. Re was separated from this solution using an anion exchange resin (1ml Dowex 1X8, 100-200 mesh size, pre cleaned with 6N HCl and 8N HNO_3) conditioned in 0.8 N HNO_3 medium. After loading the sample, the resin is washed four times, each with 3 ml 0.8 N HNO_3. The Re from the column was eluted with 12 ml 8N HNO_3. The eluate is evaporated to near dryness and taken in 1 ml of 0.8 N HNO_3 and the Re repurified by passing through 100 μl anion exchange resin. The column is washed thrice, each time with 0.5 ml 0.4N HNO_3. The Re from the column is eluted with 3 ml 8N HNO_3. The solution containing Re is evaporated to dryness, digested with a

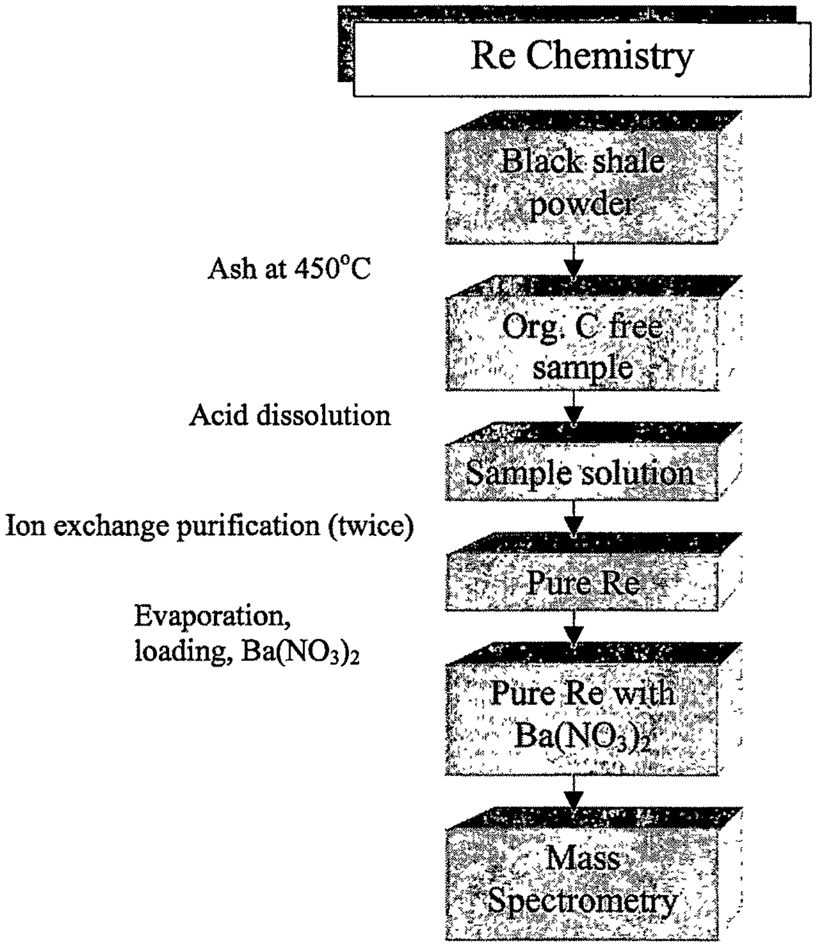


Fig. 2.7: Flow chart for the Re chemistry

drop of conc. HNO_3, dried and taken in 0.2 N HNO_3 (~0.5 μl). A part of this solution is loaded on the filament for mass spectrometric measurements. In a few black shale samples Re concentration was measured by wet oxidation and after ashing. The results (Table 2.4) are consistent within errors, suggesting that there is no measurable loss of Re during the ashing processes.

Further, a few control experiments were done to determine the optimum temperature for ashing. Towards this, a few black shale samples were ashed at three different temperatures. The results (Table 2.5) show that samples ashed between 450-600°C all yielded Re concentrations which are within errors. Based on these results we maintained an ashing temperature of 450°C for ~12 hrs, as it was the minimum.

Table 2.4: Inter-comparison of Re measurements

Sample	Re (ng g^{-1}) (a)	Re (ng g^{-1}) (b)
KU92-56(1)	255 ± 18	266 ± 6
KU92-56(2)	264 ± 4	
KU92-58(1)	18.8 ± 0.12	18.1 ± 0.08
KU92-58(2)	18.4 ± 0.30	

a: acid digestion, b: ashing followed by acid digestion

Table 2.5: Re concentration in samples ashed at different temperatures

Sample #	Re (ng g^{-1}) 600°C	Re (ng g^{-1}) 550°C	Re (ng g^{-1}) 450°C
KU92- 49	-	5.25 ± 0.06	5.18 ± 0.2
UK94-55	0.39 ± 0.05	0.34 ± 0.02	0.36 ± 0.01, 0.35 ± 0.01
UK98-1	8.81 ± 0.12	-	8.64 ± 0.13
UK98-2	69.7 ± 0.28	-	68.6 ± 1.6
UK98-3	145 ± 1.2	-	153 ± 2.5
UK98-4	3.25 ± 0.08	-	3.16 ± 0.10

(d) Os and Re mass spectrometry

The 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). The NTIMS technique have been established at PRL for the measurement of Re and Os isotope composition following the available procedures. The mass spectrometer used in these studies is an indigenously built, 23 cm radius, 60° sector magnetic field, single focusing instrument equipped with faraday cup collector (Trivedi, 1990). This machine was used earlier for Rb-Sr isotope measurements (Trivedi, 1990; Trivedi *et al.*, 1995). The polarities of the magnet and ion acceleration high voltages were reversed to suit the NTIMS operation. Following is the mass spectrometric parameters used for Re and Os measurements (Table 2.6):

Table 2.6: Mass spectrometric settings for Re & Os measurements

Element	Accelerating Potential (KV)	Magnetic Field Gauss	Filament current (A)
Re	4.66	5700-5725	2.2-2.4
Os	4.87	5670-5730	2.1-2.3

The Os metal fraction on the Pt filament was removed from the degassing chamber. About 20 μg of spec. pure $Ba(NO_3)_2$ (from Spex Industries Inc., USA) as a solution was loaded on the top of the Os metal and dried at 0.5 amp to enhance the production of negative thermal ions of OsO_3 (Creaser *et al.*, 1991). This was loaded in the mass spectrometer and kept overnight to pump down to the required vacuum. The mass spectrometric measurements of Os were carried out by bleeding oxygen into the mass spectrometer at a pressure of $\sim 2\times10^{-6}$ torr (Hauri and Hart, 1993) which is known to promote ionisation efficiency of OsO_3^- and ReO_4^-. Typical ion currents were about 10^{-13} A at mass 240 per 100 pg Os load. Os isotopic ratios were measured at masses 240($^{192}Os^{16}O_3^-$), 238($^{190}Os^{16}O_3^-$), 237($^{189}Os^{16}O_3^-$), 236($^{188}Os^{16}O_3^-$), 235($^{187}Os^{16}O_3^-$) and 234($^{186}Os^{16}O_3^-$). Backgrounds were measured at masses 233.5 and 240.5. The oxide ratios were corrected for interferences from ($Os^{16}O_2{}^{17}O^-$) and ($Os^{16}O_2{}^{18}O^-$) and mass dependent isotope fractionation using $^{188}Os/^{192}Os$ abundance ratio of 0.32439 (Nier, 1937) to obtain elemental isotope ratios. In addition, corrections for Os isotope contributions from the spike were also made. A typical spectrum of Os standard and Os extracted from one of the black shales is shown in Fig. 2.8.

For Re also, ~ 10 μg of $Ba(NO_3)_2$ solution was loaded on the top of it on the Pt filament and placed in the mass spectrometer for analysis. Typical ion current for a 100 pg load Re standard was about 5×10^{-13} A at mass 251. In sample loads the currents were

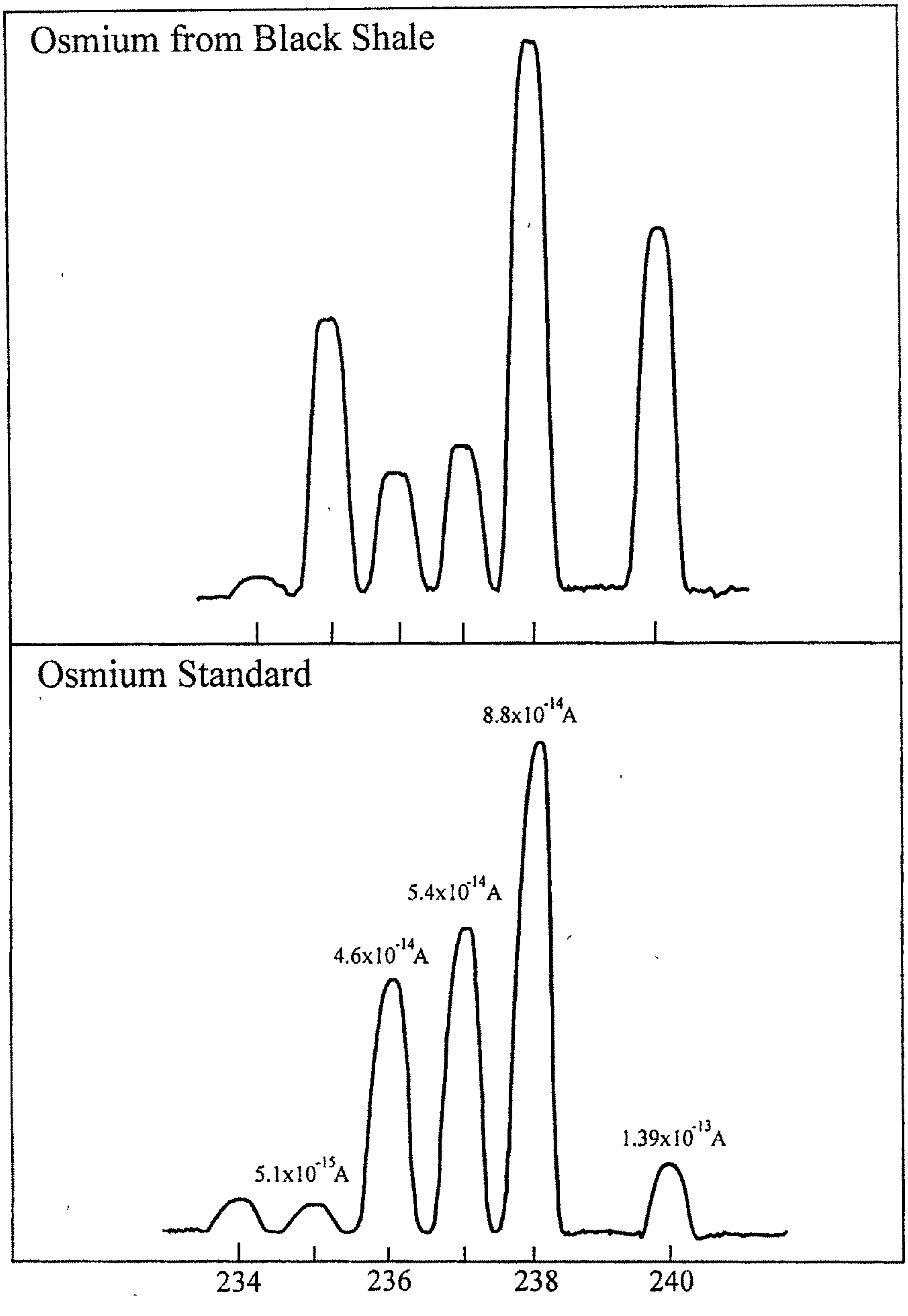


Fig.2.8 Typical mass spectrum obtained from NTIMS for Os derived from black shale (top) and Os standard (bottom)

lower 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 ($^{185}Re\ ^{16}O_3{}^{18}O^-$ on $^{187}Re^{16}O_4^-$) were made for calculating Re concentration. The Os and Re data reduction procedures followed those being used at Yale and WHOI (Williams and Ravizza pers. comm.).

Table 2.7: Os isotopic composition of standard with time

Date	Standard (pg)	$^{187}Os/^{186}Os$	$^{190}Os/^{192}Os$
05.12.1997	1025	0.8751 ± 0.0062	0.6424 ± 0.0024
06.12.1997	470	0.8973 ± 0.0080	0.6451 ± 0.0012
13.12.1997	100	0.9075 ± 0.0234	0.6455 ± 0.0115
22.12.1997	300	0.8766 ± 0.0125	0.6422 ± 0.0019
17.01.1998	250	0.8872 ± 0.0096	0.6446 ± 0.0007
19.01.1998	200	0.8926 ± 0.0099	0.6469 ± 0.0010
09.02.1998	250	0.8915 ± 0.0064	0.6462 ± 0.0025
01.04.1998	400	0.8790 ± 0.0068	0.6430 ± 0.0011
04.06.1998	60	0.8912 ± 0.0087	0.6431 ± 0.0013
10.11.1998	2000	0.8860 ± 0.0009	0.6439 ± 0.0002
Mean		**0.8884 ± 0.0198**	**0.6441 ± 0.0033**
Martin (1990)		0.897 ± 0.016	0.6417 ± 0.0075
Luck and Allegre(1983)			0.64382

Table 2.7 lists the isotopic composition of Os measured over several months in standard loads. The standard loaded are within ± 10% of the values given. 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 $^{187}Os/^{186}Os$ and $^{190}Os/^{192}Os$ in the standard runs are 0.8884 ± 0.0198 and 0.6441 ± 0.0033 respectively in agreement within errors with those reported (Table 2.7). Individual errors (within run) are $\pm 2\sigma$ uncertainty on the mean whereas the error given for the mean is twice of standard deviation calculated from the ten numbers listed in the table for both $^{187}Os/^{186}Os$ and $^{190}Os/^{192}Os$.

The ^{185}Re/^{187}Re ratio measured in the standard is 0.594 ± 0.003, consistent with reported values within errors and are reproducible within ±0.5%. The precision of Re concentration measurements (±2 s.d. within runs) is typically ~2-3% and the reproducibility, based on replicate analysis of six pairs of samples, show excellent agreement within experimental uncertainties.

(e) Procedural blanks

Four procedural blanks for Os were run for the NiS fusion and wet chemistry using 250-500 mg Ni. It includes all steps starting from fusion, dissolution of bead, filtration, distillation, grain chemistry and loading. The sample-powdering step is not included in the blank run, but this unlikely to contribute to blank as utmost care was taken to avoid any metal contact with the samples during this process. The Os blank for the entire procedure (Table 2.8) ranged between 0.7 to 4.2 pg with an average 1.8 ± 1.6 pg. Os isotopic measurements could not be made on these blanks, as the Os load on the filament were quite low (≤1 pg). Re blank comes mainly from the Pt filament (Hauri and Hart, 1993). We ran four procedural blanks for Re; it ranged from 1.7 pg to 4.5 pg, with a mean of 3.5±1.2 pg (Table 2.8). Re and Os blanks were run four times during the study, they are listed in Table 2.8.

Table 2.8: Procedural blanks of Re and Os

Element	Date	Blank (pg)	Element	Date	Blank (pg)
Os	06.11.1997	4.2	Re	14.10.1997	1.7
	01.01.1998	0.7		15.03.1998	3.8
	21.01.1998	0.8		16.03.1998	4.5
	12.06.1998	1.6		26.08.1998	3.9
Mean		1.8 ± 1.6	Mean		3.5 ± 1.2

(f) Precision and accuracy of Re and Os measurements

Inter laboratory comparison

To check the accuracy and precision of the entire procedure, NiS fusion and wet chemistry, we analysed two samples of black shales of known Os and Re concentrations and isotope composition. These samples were obtained from Dr. G. Ravizza and their Os and Re analysis were made earlier by the SIMS technique (Ravizza, 1991 and pers. comm.). Table 2.9 lists the inter-comparison between the two sets of measurements which shows reasonable agreement.

Table 2.9: Os & Re concentrations and ^{187}Os/^{186}Os ratio in black shales : Inter laboratory comparison

Sample	[Re] ng g^{-1}	[Os] pg g^{-1}	^{187}Os/^{186}Os
NA10			
Present study	119.9	904	67.00 ± 0.51
Ravizza (1991)	119.7	943	70.26 ± 0.74
NA11			
Present study		7390	69.19 ± 0.54
Ravizza (1991)		7374	67.98 ± 1.02

Table 2.10: Results of Re, Os and ^{187}Os/^{186}Os repeat measurements

Sample	Re (ng g^{-1})	Os (ng g^{-1})	^{187}Os/^{186}Os
UK98-1(i)	8.81 ± 0.24	0.60 ± 0.01	15.373 ± 0.093
(ii)	8.64 ± 0.26	0.60 ± 0.04	15.439 ± 0.108
UK98-2(i)	69.7 ± 0.57	1.57 ± 0.04	30.490 ± 0.164
(ii)	68.6 ± 3.13	1.45 ± 0.05	30.464 ± 0.154
UK98-17(i)	-	2.84 ± 0.08	31.853 ± 0.179
(ii)	-	2.95 ± 0.06	31.494 ± 0.072
KU92-56(i)	255 ± 18	13.2 ± 0.40	18.098 ± 0.218
(ii)	264 ± 4	13.5 ± 0.35	18.002 ± 0.134
(A)	266 ± 6	-	-
KU92-58(i)	18.8 ± 0.12	0.79 ± 0.002	19.864 ± 0.139
(ii)	18.4 ± 0.30	0.80 ± 0.004	19.869 ± 0.070
(A)	18.1 ± 0.08	-	-

All Re measurements by ashing followed by acid digestion, except in KU92-56 and KU92-58, where measurements were made by both the procedures; (i) and (ii) refer to wet oxidation and (A) ashing followed by acid digestion.

Reproducibility

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 2.10) show good agreement between the replicates.

(ii) Rb & Sr Measurements

Measurements of Rb and Sr abundances and Sr isotopic composition in carbonate samples from the Lesser Himalaya were made using Thermal Ionisation Mass Spectrometer (TIMS). Sr isotopes were measured both in the whole rock and their mild acid leachates (Singh *et al.,* 1998). For the whole rock analysis, about 100 mg of powdered samples were brought to solution by digesting them in HF-HNO_3. The solution were spiked with ^{87}Rb, ^{84}Sr tracers, and the tracers were equilibrated with sample by heating them in closed containers and dried. The dried residue was taken in 2.5 N HCl and Sr and Rb were separated and purified by cation-exchange (Dowex 50X8, 200-400 mesh) following the procedures used in our laboratory (Trivedi, 1990). The separated Rb and Sr fractions were dried, taken in a drop of orthophosphoric acid and evaporated directly onto an outgassed tantalum filament of the ion source (Trivedi 1990). To determine the isotope ratios of the carbonate fraction, the whole rock samples were leached using either dilute acetic acid or hydrochloric acid (Singh *et al.,* 1998). For the acetic acid leach, about 100 mg of powdered samples were treated with 20 ml of 5% acid at 60°C for 1 h. The slurry was cooled, let stand for 2-3 h and centrifuged. For hydrochloric acid leach ~ 100 mg of the powdered samples (or in some cases ~ 1 gm of a few mm size chips) were treated with ~20 ml of 0.1 N HCl at room temperature for 1-2 h and centrifuged. The leachates were dried, taken in 2.5 N HCl and Rb, Sr are separated and further purified by ion exchange procedure. The purified Rb and Sr were run for their isotopic composition using 9" radius single focussing mass spectrometer fitted with faraday cup collector and the ion current was recorded digitally.

The Sr isotopic ratios were normalized to $^{86}Sr/^{87}Sr = 0.1194$. The long-term stability of the mass spectrometer was checked by measuring the ratio $^{87}Sr/^{86}Sr$ of NBS-987 standard periodically. The mean $^{87}Sr/^{86}Sr$ value of the standard, over the past few years being 0.71025 ± 0.00007. The overall precision in the determination of $^{87}Sr/^{86}Sr$ is

± 0.0005 (two standard error on the mean based on ~50 measurements). These error are quite small compared to the scale of Sr isotope variation in carbonates analysed (Trivedi *et al.*, 1995; Singh *et al.*, 1998). In addition, to check on the accuracy of $^{87}Sr/^{86}Sr$ measurements sample of seawater from the Arabian Sea and $CaCO_3$ from a living coral from the Lakshadweep were analysed (Trivedi *et al.*, 1995). These analyses yielded $^{87}Sr/^{86}Sr$ of 0.7097 ± 0.0006 and 0.7092 ± 0.0002, respectively, in good agreement with contemporary seawater values. The total Rb and Sr procedural blanks were ~0.5 ng and ~4 ng respectively (Trivedi *et al.*, 1995).

(iii) O & C isotopes measurements

The oxygen and carbon isotope measurements were made in the stable isotope mass spectrometry group. The oxygen and carbon isotopes were measured in the CO_2 liberated from ~5 mg of samples by treating them with 100% phosphoric acid for ~72 h. The measurements were made using a VG 903 mass spectrometer with respect to a laboratory standard calibrated against V-PDB. The precision for $\delta^{18}O$ and $\delta^{13}C$ measurements are ±0.2‰ (Sarkar *et al.*, 1990). The $\delta^{18}O$ and $\delta^{13}C$ data are expressed with respect to V-PDB, without any additional fractionation correction for $\delta^{18}O$ in dolomite.

(iv) Determination Elemental Abundances

(a) Sample preparation for elemental analysis

The chemical composition of carbonates and black shales were measured using either AAS or ICP-AES techniques. A common sample preparation procedure was followed for these measurements. For the whole rock analysis of black shales, 0.5 to 1 g of samples were dissolved using HF, $HClO_4$, HNO_3 and HCl. The samples were brought in to solution using 1N HNO_3. For the carbonate whole rock measurements, samples were first treated with dilute HCl to dissolve the carbonate and after the reaction was over, the slurry was centrifuged. The solution was carefully decanted into a beaker. The residue was transferred to Teflon beaker quantitatively and brought into solution after treatment with HF, HNO_3, HCl. This solution was mixed with the superanate collected earlier, dried and taken in 1N HNO_3 for elemental measurements. For the carbonate leach measurement ~ 1g of the sample powder was treated with ~200 ml of 0.1 N HCl for 1-2 h at room temperature with occasional stirring, The slurry was centrifuged, the superanate was made to known volume and analysed to yield elemental composition of the carbonate phase. In a few samples the residue of the 0.1N HCl leach were treated with HF, HNO_3, HCl and brought to solution. These solutions were also analysed separately. The elemental composition was measured either by AAS or ICP-AES. Few of the elements were measured by both the techniques. In the following section, measurement details using the AAS and ICP-AES are discussed.

(b) Atomic Absorption Spectrophotometry

The elemental analyses of carbonates, black shales and river water samples were done using atomic absorption spectrophotometer, Perkin Elmer models 305 and 4000, following our laboratory procedures (Sarin *et al.*, 1979; Sarin *et al.*, 1992). The instruments were calibrated using either single or multi-element laboratory standards. Wherever required the sample solutions were suitably diluted to bring the concentration to the linear portion of the absorption curve. To check the accuracy, USGS standard, W-1, was run along with the samples for several elements and the results are given in Table 2.11

Table 2.11: Results of USGS standard, W-1

Element	Measured	Recommended*
Fe (%)	8.0	7.79
Mg (%)	3.81	3.99
Ca (%)	7.6	7.82
Na (%)	2.17	1.57
Al (%)	7.63	7.86
Cu (ppm)	124	121
Mn (ppm)	1346	1364

* From Potts *et al.* (1992)

Few samples are run in duplicate to assess the reproducibility, these results are given in Table 2.12. Based on these duplicate analyses the coefficient of variation for the AAS measurements were calculated using the formula,

$$CV(\%) = \left(\frac{1}{2n} \sum \left(\frac{d_i}{x_i} \right)^2 \right)^{\frac{1}{2}} \times 100$$

where d_i is difference between the duplicates with mean x_i and n is the total sets of duplicates. The results are given in Table 2.13.

Table 2.12: Replicate measurements of different elements in black shales using AAS

Sample	Fe(%)	Mg(%)	Ca(%)	Na(%)	K(%)	Al(%)	Mn(ppm)	Cu(ppm)
KU92-10(1)	8.02	1.28	0.37	0.37	7.02	10.61	37	2
(2)	7.52	1.36	0.23	0.28	6.36	9.83	35	2
KU92-17(1)	2.29	1.53	0.28	0.81	3.54	9.51	57	15
(2)	2.26	1.50	0.25	0.61	3.30	9.38	59	12
KU91-39(1)	4.61	2.80	0.13	0.49	3.99	10.34	269	10
(2)	4.56	2.80	0.13	0.55	4.14	10.45	264	12
KU92-41(1)	3.64	1.75	0.15	1.21	2.81	9.62	258	13
(2)	3.93	1.80	0.16	1.46	3.04	9.78	262	15
KU92-53(1)	0.30	0.45	0.92	0.15	0.30	0.47	100	23
(2)	0.26	0.46	0.97	0.12	0.30	0.51	104	23

Table 2.13: Coefficients of variation for different elements for AAS measurements

Element	Coeff. Var.(%)
Fe	5.5
Mg	2.3
Ca	15.4
Na	15.9
K	4
Al	3
Mn	2.5
Cu	10

(c) Inductively Coupled Plasma- Atomic Emission Spectrophotometry

Elemental composition in some of the carbonate samples were measured using a Jobin Yvon ICP-AES (model 38S;) in sequential mode. The instrument was calibrated using either commercially available or laboratory made multi-element standards. Several USGS standards were analysed to check the accuracy of the measurements. The results are given in Fig. 2.9. The concentrations measured in the USGS standards are in good agreement with those reported (Potts *et al.*, 1992). During the course of this work a few of the black shale samples were analysed for their elemental concentrations both by ICP-AES and by AAS. The comparison of results shows (Fig. 2.10) that the concentrations of various elements obtained by both the techniques are in excellent agreement.

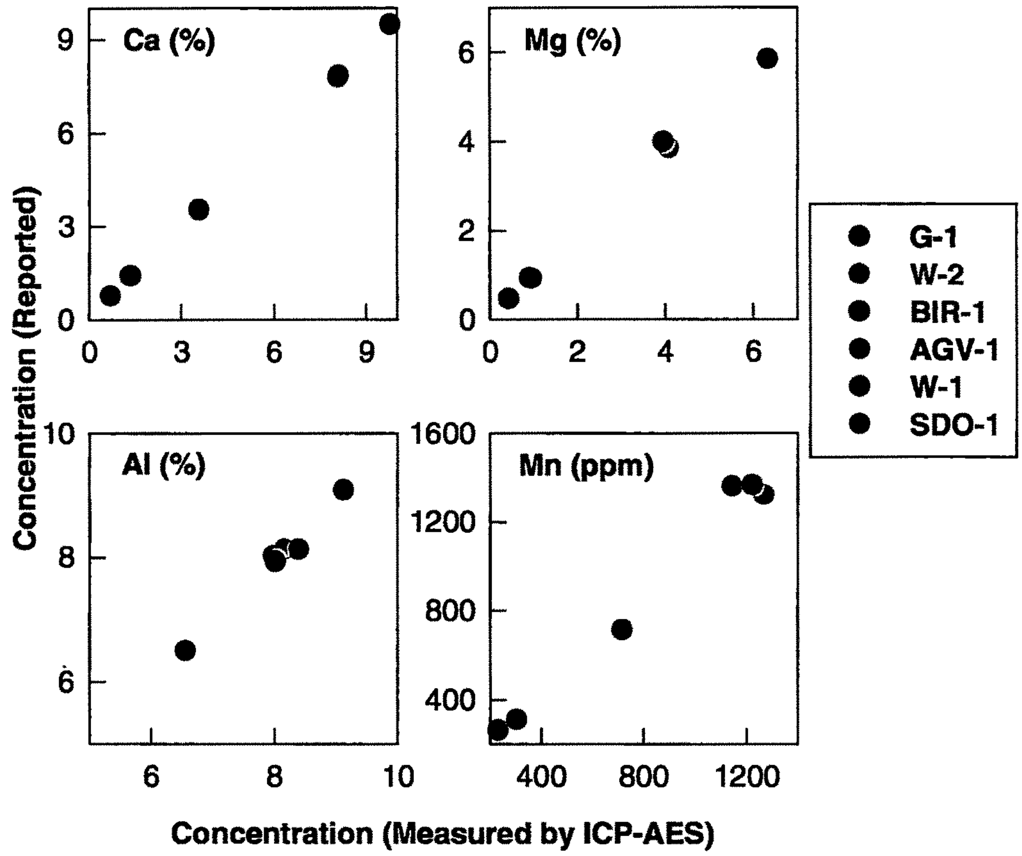


Fig. 2.9: Comparison of measurement made with ICP-AES with reported values for different USGS standards. Reported concentration are from Potts *et al.* (1992)

In carbonates, Sr concentration were measured by isotope dilution mass spectrometry. In a few samples, it was also measured using ICP-AES. The comparison of

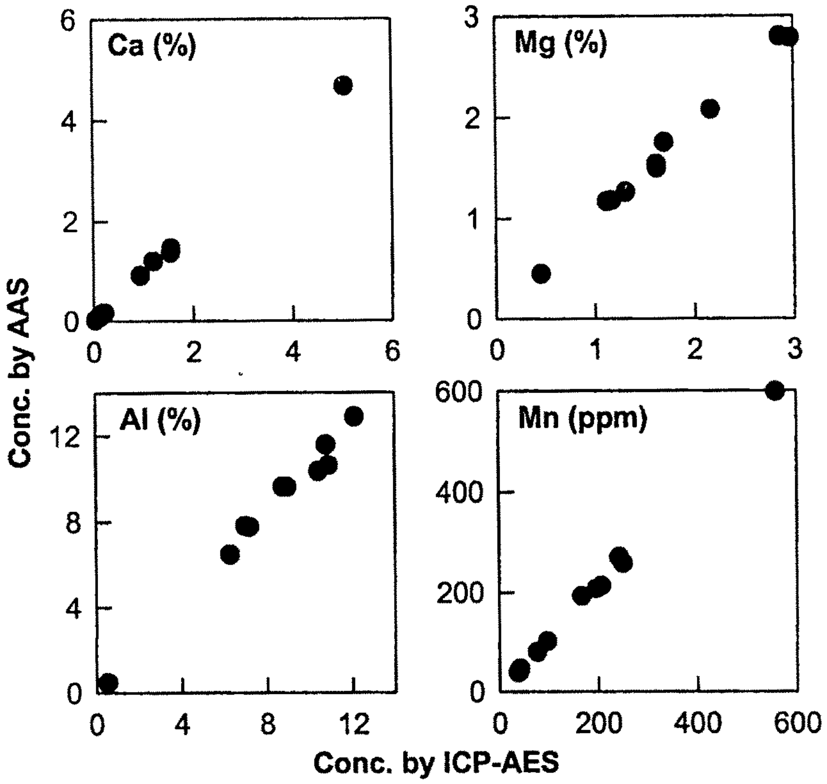


Fig. 2.10: Comparison of concentration of various elements in black shales measured by ICP-AES and AAS.

TIMS and ICP-AES data is shown, Fig. 2.11. The two techniques show good agreement particularly in lower concentration range, though the ICP-AES values are generally lower by ~10%.

(d) UV-Visible Spectrophotometry

Phosphorus in the black shales and dissolved silica in the river water samples were measured using a Beckman UV-visible spectrophotometer, model 26. Dissolved silica was measured using the molybdenum blue method (Strickland and Parsons, 1968). Phosphorus measurements in the black shale were done by dissolving ~0.5 g samples using HF, $HClO_4$, HNO_3, HCl acids. An aliquot of the solution was used for P determination using molybdenum blue method (Strickland and Parsons, 1968). The concentration-absorption curve was established with known phosphorus standards. USGS standard W-1 was run with the samples. The P measured in W-1 was 619 ppm, this compares well with the recommended value of 611 ppm (Potts *et al.*, 1992). Few black shale samples were run in duplicate. They are given in Table 2.14.

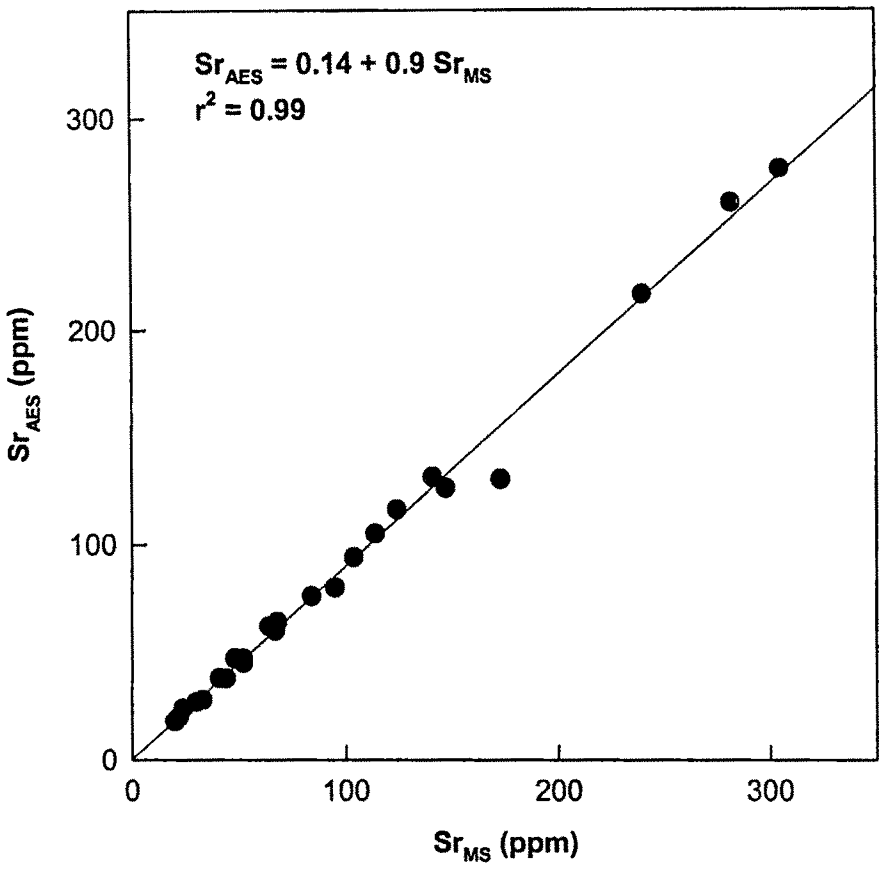


Fig. 2.11: Sr in carbonates, measured by isotope dilution mass spectrometry and by ICP-AES

Table 2.14: Replicate analyses of phosphorus in black shales using spectrophotometer

Samples	P (ppm)
KU92-10(1)	957
(2)	1039
KU92-17(1)	738
(2)	695
KU92-39(1)	365
(2)	370
KU92-41(1)	460
(2)	464
KU92-53(1)	493
(2)	521

Based on the above replicate results, the coefficient of variation of P measurements is calculated to be 3.7%.

Dissolved silica in river waters was measured directly from filtered water samples. Typically 5 ml samples were used for each measurements. In addition, silica concentration in a few water samples was measured by both spectrophotometry and ICP-AES. The results are given in Table 2.15:

Table 2.15: Silica concentration in river waters (μM ℓ^{-1}) by spectrophotometer and ICP-AES

Sample #	SiO_2 Concentration (a)	(b)
RW96-1	111 ± 0.7	110 ± 0.8
RW96-7	56 ± 0.3	56 ± 0.7
RW96-10	265 ± 1.5	277 ± 7
24/89	118 ± 0.7	120 ± 1.5

(a): by Spectrophotometry and (b): by ICP-AES

The errors in spectrophotometry measurements are ± 1 sigma uncertainties in the calibration. Therefore it represents the minimum error. Errors given on ICP-AES measurements are standard deviations based on three measurements of the same aliquot.

(e) Inorganic, Organic carbon and Nitrogen analysis

Total carbon and nitrogen contents in the samples were measured using a CN analyser (FISONS model NA1500; Sarin *et al.,* 1997) while the inorganic carbon ($CaCO_3$) using a coulometer. For CN analysis ~20 mg of samples were packed in tin cups and combusted in the furnace of CN analyser in presence of chromium trioxide and silver cobaltous cobaltic oxide catalysts. The evolved CO_2 was purified from the combustion products on chromatography column and measured by thermal conductivity detector. The measured CO_2 provides measure of total carbon (organic + inorganic) in the sample. The analyser was calibrated using Deer-River black shale standard and checked for its accuracy using shales of known carbon concentration. In addition, to check the precision of the measurements several black shale samples were run in duplicate for total carbon and $CaCO_3$ by coulometer (Table 2.16).

Table 2.16: Replicate measurements of total carbon and inorganic carbon in black shales

Sample	Total C (%)	Inorganic Carbon(%)
KU92-8(1)	3.47	
(2)	3.45	
KU92-17(1)	0.71	
(2)	0.68	
KU92-51(1)	1.57	
(2)	1.61	
KU92-56(1)		1.01
(2)		0.99
UK94-55(1)	1.63	
(2)	1.60	
HP96-26(1)	0.67	
(2)	0.65	
UK98-2(1)	5.57	
(2)	5.82	
UK98-9(1)		1.27
(2)		1.29
UK98-20(1)	6.89	5.08
(2)	6.80	5.08

To measure the inorganic carbon ~ 50 mg of black shale samples were treated with 30% phosphoric acid in a test tube and the liberated CO_2 was measured by coulometer. The duplicate analyses of the samples are given in Table 2.16.

The coefficient of variation for total carbon measurements is ~2% and that for inorganic carbon measurements is 1% calculated based on the replicate measurements (Table 2.16). From these measurements, the abundance of organic carbon in the sample was calculated as:

$$C_{org} = C_T - C_I$$

where C_T is the total carbon and C_I is the inorganic ($CaCO_3$) carbon.

(f) Anion measurements by ion chromatography

The anions Cl, SO_4, NO_3 and F in river water samples were measured using ion chromatograph, (Dionex model # Series 2000*i*-SP). For analyses, Dionex IonPac AS4A separator column coupled with AG4A guard column were used. Samples were injected in the column where the anions were separated based on their retention time and then they were selectively eluted and their conductance were measured to determine their concentrations. The system was calibrated using multi-anion working standards. The overall precision of measurements is ~5% (Sarin *et al.,* 1992).

(g) Mineralogical Studies

Carbonate samples were analysed for their mineralogy using Philips X-ray diffractometer and thin section microscopy. For X-ray analysis, sample powders were mounted on Al holder and scanned between 20°-60° using copper $K\alpha_1$ radiation as X-ray source. Along with samples standards of dolomite (Thornwood, New York), calcite, limestone braccia (Boulder County) and quartz (Park County, Colorado) acquired from Ward's Natural Science Establishment, Inc., Rochester, N.Y. and a coral sample from Gulf of Kutch were also run. Various minerals present in the samples were identified based on the peaks.

Thin section studies of carbonate samples were done to study their petrography, effects of alteration (cements, veins) and presence of opaque minerals. Few of the thin sections were made at Indian Institute of Technology, Kharagpur (courtesy Prof. Amitabh Chakraborty) and others were made at Geological Survey of India, Gandhinagar. The microscopic studies of these thin sections were done using NICON UFX - 11A microscope at the Department of Geology, University of Delhi, Delhi under supervision of Prof. S.K. Tandon.