

Major ion chemistry of Renuka Lake and weathering processes, Sirmaur District, Himachal Pradesh, India

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Abstract Renuka Lake in the Lesser Himalaya, Himachal Pradesh is in a valley surrounded by mountains comprised of highly crumpled, shattered, crushed, folded and dislocated rocks consisting of carbonaceous shales–slates often pyrite-ferrous, limestone, quartzites, boulder beds, etc. A detailed and systematic study of the major ion chemistry of the lake, clay mineral composition of the bed and core sediments and the Pb^{210} isotope estimation in the latter was conducted. The chemistry is dominated by carbonate weathering and (Ca + Mg) and ($HCO_3 + SO_4$) accounts for about 90% of the cations and anions. The SO_4 content is almost the same as the HCO_3 . The low contribution of (Na + K) to the total cations and the (Ca + Mg) and HCO_3 data tends to indicate that silicate weathering has not been the potential source of major ions to the lake waters. This difference may be related to the increasing susceptibility to weathering of carbonate over silicate rocks exposed in the catchment and also seepage of water at the bottom. The high sulphate content in waters is derived from dissolution of pyrite-ferrous reduced black shales, which constitute a significant lithology in the catchment. The chemical index of alteration (CIA) value in core sediments is on an average 76, which is comparable with average shale (70–75) and the rate of sedimentation 3.3 mm/year based on measurement of Pb^{210} , indicating a fairly high weathering rate in the catchment. Illite is the dominant clay mineral (52–90%) in the bed and core sediments, chlorite constitutes 7–48% and the kaolinite–chlorite mixed silicate layer is 1–2%. This is consistent with the shale–slate, sandstone lithology in the valley.

Keywords Black-shale · Carbonate weathering · Major ion chemistry · Pyrite-ferrous · Renuka Lake

Introduction

The major ion chemistry of lake waters reveals the nature of weathering of the catchment lithology, soil erosion on the hill slopes, rate of sedimentation, etc. Renuka Lake is a wetland that has been declared for special conservation by the Ministry of Environment and Forests, Government of India; hence, it is of national and international importance. However, no comprehensive geochemical data for the waters and sediments are available for this lake. A few sketchy reports containing general parameters of the lake waters have been compiled by Agrawal and Thakur (1981). Unlike in rivers, where the weathering intensity is assessed based on either solute concentrations or fluxes, in lakes, being a ponded water body, the former is significant and the rate of sedimentation reveals the discharge. Climatic impacts on chemical weathering must ultimately cause fundamental differences in the thermodynamic and kinetic interactions between minerals and solutions. The volume of water in a lake and, consequently, the level of its surface, depend on the inputs and outputs of water balance. If there is a good balance, the water level fluctuates very little. However, because of year-to-year changes in rainfall and other climatic factors some fluctuation is expected. In the present investigation a detailed geochemical study of Renuka Lake was carried out to identify the sources of major ions to the lake in terms of atmospheric supply, chemical weathering of catchment lithology, soils of the drainage basin and groundwater, and to study the clay mineralogy of the sediments to understand the relationship between mineralogy and water chemistry.

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Geomorphic features and geology of the area around Renuka and its catchment

Renuka Lake is about 35 km from Nahan and 125 km from Chandigarh (Fig. 1). The oval-shaped lake has a water spread of 670 ha at an elevation of 620 m and bound by

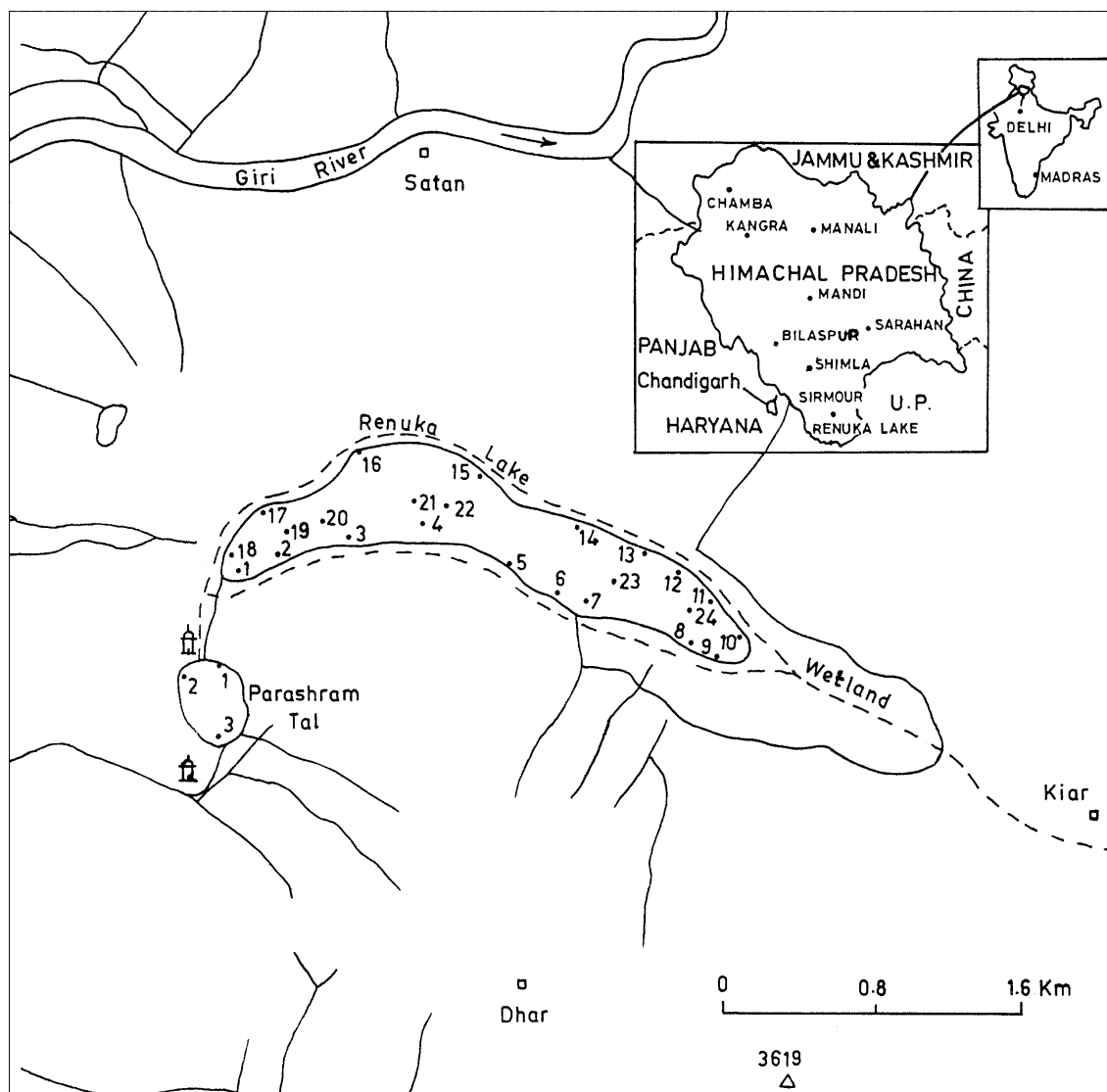


Fig. 1

Location of sites of samples collected in Renuka Lake and Parashram Tal Sirmour District, Himachal Pradesh

$30^{\circ}36'30''N$ latitude and $77^{\circ}27'6''E$ longitude. The lake follows a riparian course between two steep hill slopes with forest; and this and the Parashram Tal are the two lakes close by along the abandoned course of the Giri River in the Sirmour district. Inlets to the lake are watersheds, rainwater runoff from the catchment and underground seepage. The maximum length of Renuka is 1,050 m and its maximum breadth is 204 m. The maximum depth is about 13 m. The catchment area is ~ 254.3 ha. The annual rainfall in this region is between 150 and 199.9 cm (Joshi 1984).

The rocks of Jaunsar, Blaini, Infra-Krol, Krol Groups (neo-Proterozoic-Proterozoic) constitute the geology of this region (Auden 1934). This has been rendered highly complicated because of intense tectonic movements and development of the Krol-Giri thrust causing intense crushing, fracturing, folding and dislocation of outcrops. As a consequence the lithological units are highly crumpled and mixed, and are often referred to as undifferentiated.

Almost each unit of the Krol Group, Mandhalis and Blainis are limestone dominated and the catchment rocks of Renuka are represented by Infra-Krol dark shales, slates, black carbonaceous shales or slates and slaty quartzites. Purple-red shales with intercalation of green shales, thin dolomitic and cherty limestones of the Krol Group and Blaini boulder bed with limestone and well-bedded greyish white limestone and shales of the Krol Group are the common rock types of the catchment (Fig. 2). The Infra-Krol shale and slates are rich in iron and are seen as seepages of ferric hydroxide, and white incrustations of ferric sulphate and chloride that cover the surface of these rocks. The parent mineral must have been pyrites (Auden 1934). In thin sections, sericite, quartz, pyrite and in some cases chlorite, and in slaty quartzite, carbonates are also present. There is a large quantity of carbonaceous dust in these rocks. In fact, the water and sediment chemistry of Renuka Lake reflects a degree of susceptibility of the complex lithological setup to weathering of the region, which is unique compared with other lakes. The soil composition of this region reflects the heterogeneous mixture of carbonate rocks, sandstones, shale, and silt

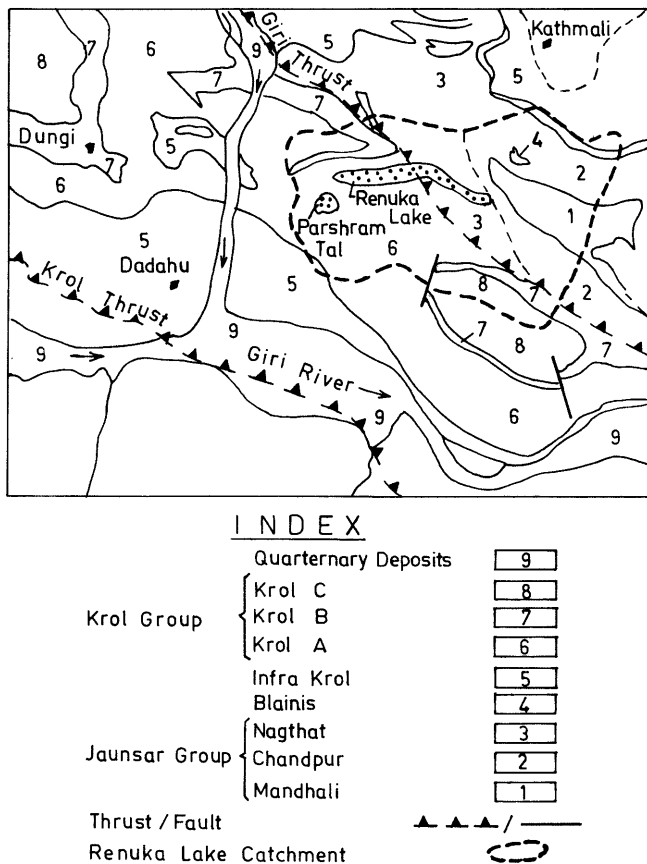


Fig. 2

Map showing drainage and lithology around Renuka Lake Himachal Pradesh. 1 Boulder bed and limestone; 2 slates; 3 quartz arenite with conglomerate; 4 boulder bed and dolomite; 5 carbonaceous slates; 6 argillaceous limestone and shale; 7 red shale with limestone lenses; 8 crystalline blue-grey limestone

stone in various proportions (Srikantia and Bhargava 1998).

Methodology

Renuka Lake water samples were collected in the months of March–April from several locations traversing on boat in order to cover the entire lake, and that of Parashram Tal was sampled from the banks because of constraints of boat facilities (Fig. 1). The samples were filtered and stored in polyethylene bottles. The pH, electrical conductivity (EC), dissolved oxygen (DO), total dissolved solids (TDS) and redox potential (ORP) were measured at the site within a few hours of collection of samples with the help of a portable field kit. The carbonate and bicarbonate were measured by acid titration, chloride by AgNO_3 titration, sulphate by $\text{Ba}(\text{ClO}_4)_2$ titration after passing the samples through a cation exchange resin, phosphate by an ascorbic acid method using a spectrophotometer; Ca and Mg by a Perkin–Elmer Spectrophotometer 2100 and sodium and potassium by an EEL Flame Photometer. The grab sediment samples were taken with the help of an auger from shallow depth, and core samples by inserting a long PVC

pipe and pushing it down as far as possible. The Pb^{210} estimation was done by processing the samples and counting activity using a windowless gas-flow beta counter. The clay mineral analysis was carried out by XRD on $<2\text{-}\mu\text{m}$ sized sediment fractions.

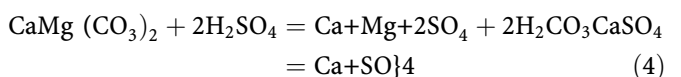
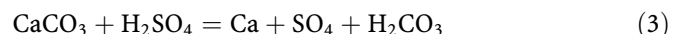
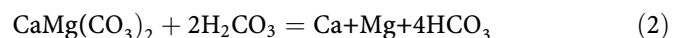
Major ion chemistry and chemical weathering processes

The major ion composition data of Renuka Lake and Parashram Tal are given in Table 1. The analytical precision for the measurement of major ions is better than $\pm 5\%$. The observed charge balance between cations (T_z^+) and anions (T_z^-) is further proof of the precision of these data (Table 2). Statistical analysis of the data shows that the T_z^+ and T_z^- are coupled by the relation $T_z^+(\mu\text{Eq/l}) = 1.09T_z^-(\mu\text{Eq/l}) + 0.59$ with a correlation coefficient of 0.97 for 21 data points. This implies that the contribution of ions other than those measured are insignificant for the cation and anion charge balance. For instance, PO_4^{3-} content is negligible and other ions such as NO_3^- in the lake water samples are quite low (Tables 1 and 2).

Discussion

The source of dissolved materials in the lake seems to be primarily weathering of rocks and precipitation. Gibbs (1970) argues that the latter is of overwhelming importance and observes that if the TDS is plotted against $\text{Na}/(\text{Na} + \text{Ca})$ for continental waters, a distinct 'boomerang' pattern results. Samples of Renuka Lake fall in the rock dominance field close to TDS (Fig. 3), suggesting that the weathering of rocks primarily controls the major ion chemistry of lake waters.

The results of the present study on the dissolved and suspended phases of the Renuka has been synthesised to determine the source of major ions to the lake waters and their relation to regional geology and weathering processes. The abundance of dissolved major cations (Na, K, Mg and Ca) and anions (HCO_3 , SO_4 and Cl) in waters can be modelled in terms of the weathering of various minerals in the drainage basin. Garrels and Mackenzie (1971); Holland (1978) and others have shown some weathering reactions for minerals such as calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$] and gypsum (CaSO_4) as follows:



A source of protons is necessary for the rapid weathering of carbonates. If the weathering is by carbonic acid, the

Table 1

Chemical characteristics of the Renuka Lake and Parashram Tal. *EC* Electrical conductivity; *ORP* Redox potential; *DO* dissolved oxygen; *TDS* total dissolved solids; *TH* total hardness

Location No.	pH	EC ($\mu\text{s/cm}$)	ORP (mV)	DO	TDS	CO ₃ ²⁻	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻ (mg/l)	PO ₄ ³⁻	SiO ₂	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TH
RN-1	8.35	554	231	7.9	360	12	109.8	130	36.92	13.5	7.20	54.00	37.6	9.44	29.73	289.65
RN-2	8.47	548	234	8.2	360	12	158.6	150	8.52	3.5	6.10	57.50	37.2	8.09	1.38	296.75
RN-3	8.52	547	232	8.1	360	18	134.2	130	9.94	5.0	6.10	44.50	36.4	7.42	1.04	260.98
RN-4	8.42	549	235	7.0	360	18	134.2	130	9.94	7.0	6.60	46.00	37.6	7.42	1.04	269.67
RN-5	8.52	548	234	6.7	360	18	146.4	152	11.36	8.5	6.20	63.50	36.9	8.09	1.04	310.50
RN-6	8.50	550	233	8.4	360	12	158.6	170	9.94	1.5	6.20	66.50	36.4	8.09	1.04	467.82
RN-7	8.51	549	236	8.1	360	18	134.2	160	11.36	13.5	6.25	59.50	37.6	7.75	0.69	303.39
RN-8	8.55	552	237	8.6	360	12	146.4	190	11.36	15.5	6.10	63.00	35.8	7.42	1.04	304.73
RN-9	8.21	552	239	9.1	360	18	146.4	135	11.36	5.5	6.25	55.50	37.2	8.09	0.69	291.75
RN-10	8.40	550	237	8.6	360	18	146.4	120	9.94	1.5	6.24	48.00	36.4	8.09	0.69	269.72
RN-11	8.59	547	235	8.9	360	24	134.2	155	9.94	3.5	6.10	59.50	37.4	7.42	0.69	302.51
RN-12	8.55	545	236	9.9	360	18	146.4	150	11.36	3.5	5.88	57.50	38.7	7.08	0.69	302.92
RN-13	8.40	544	238	10.0	360	12	146.4	150	11.36	12.0	5.70	58.00	37.2	6.77	0.35	297.99
RN-14	8.40	545	241	8.0	360	18	134.2	160	9.94	8.5	6.20	59.00	38.0	7.42	0.69	303.79
RN-15	8.51	541	236	9.2	360	12	158.6	140	9.94	5.0	6.00	58.00	36.6	6.07	0.69	295.53
RN-16	8.42	540	236	9.6	360	24	134.2	140	11.36	1.5	6.10	64.00	36.8	6.07	0.69	311.34
RN-17	8.40	531	238	9.5	350	24	122.0	135	11.36	5.0	6.10	51.50	36.6	6.41	0.35	279.29
RN-18	8.54	523	240	8.6	350	24	122.0	140	9.94	8.5	6.20	60.50	39.4	8.77	0.69	313.30
RN-19	8.38	524	246	8.4	350	00	170.8	150	12.78	3.5	6.00	56.40	37.2	10.14	1.04	294.00
RN-20	8.35	525	240	8.5	340	24	134.8	140	12.78	10.0	6.24	54.00	37.6	9.44	1.04	289.65
RN-21	8.35	523	237	8.1	330	24	146.4	140	9.94	5.0	6.08	56.00	37.2	9.44	0.69	293.00
RN-22	8.34	523	232	8.2	330	18	146.4	142	10.65	1.0	5.78	57.60	36.2	9.10	1.04	292.88
RN-23	8.34	525	229	7.5	330	12	170.8	131	10.65	7.0	5.70	52.80	38.4	8.77	0.36	289.95
RN-24	8.34	532	227	7.0	340	12	146.4	146	9.94	7.0	6.10	52.00	36.2	8.09	1.04	278.89
PRT-1	7.60	606	233	7.1	420	18	195.2	180	11.36	10.0	11.40	73.60	46.8	8.42	2.07	376.48
PRT-2	7.92	667	229	7.2	450	18	170.8	230	14.20	3.5	9.40	80.80	49.5	11.46	2.07	405.58
PRT-3	8.23	617	224	6.6	420	30	158.6	200	14.20	8.5	5.00	55.20	45.3	12.14	2.07	324.34

Table 2

Chemical composition of the Renuka Lake (meq/l)

Location No.	CO ₃ ²⁻	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	PO ₄ ³⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	T _z ⁻	T _z ⁺	$\Delta(\text{Diff})$ (T _z ⁻ -T _z ⁺)
RN-1	0.4	1.8	2.71	1.04	0.00043	2.70	3.13	0.41	0.76	5.95	7.00	-1.05
RN-2	0.4	2.6	3.12	0.24	0.00011	2.87	3.10	0.35	0.04	6.36	6.36	0.00
RN-3	0.6	2.2	2.70	0.28	0.00016	2.22	3.03	0.32	0.03	5.78	5.60	0.18
RN-4	0.6	2.2	2.70	0.28	0.00022	2.30	3.13	0.32	0.03	5.78	5.78	0.00
RN-5	0.6	2.4	3.16	0.32	0.00027	3.17	3.00	0.35	0.03	6.48	6.55	-0.07
RN-6	0.4	2.6	3.54	0.28	0.00005	3.32	3.20	0.35	0.03	6.82	6.90	-0.08
RN-7	0.6	2.2	3.33	0.32	0.00043	2.97	3.13	0.34	0.02	6.45	6.46	-0.01
RN-8	0.4	2.4	3.96	0.32	0.00049	3.15	2.98	0.32	0.03	7.08	6.48	0.60
RN-9	0.6	2.4	2.85	0.32	0.00017	2.77	3.10	0.35	0.02	6.17	6.24	-0.07
RN-10	0.6	2.4	2.50	0.28	0.00005	2.40	3.03	0.35	0.02	5.78	5.80	-0.02
RN-11	0.8	2.2	3.22	0.28	0.00011	2.97	3.11	0.32	0.02	6.50	6.42	0.08
RN-12	0.6	2.4	3.12	0.32	0.00011	2.87	3.22	0.31	0.02	6.44	6.42	0.02
RN-13	0.4	2.4	3.12	0.32	0.00038	2.90	3.10	0.29	0.01	6.25	6.30	-0.05
RN-14	0.6	2.2	3.33	0.28	0.00027	2.95	3.17	0.32	0.02	6.41	6.46	-0.05
RN-15	0.4	2.6	2.92	0.28	0.00016	2.90	3.05	0.26	0.02	6.20	6.23	-0.03
RN-16	0.8	2.2	2.92	0.32	0.00005	3.00	3.06	0.26	0.02	6.24	6.34	-0.10
RN-17	0.8	2.0	2.81	0.32	0.00016	2.57	3.05	0.28	0.01	5.93	5.91	-0.02
RN-18	0.8	2.0	2.92	0.28	0.00027	3.02	3.28	0.38	0.02	6.00	6.70	-0.70
RN-19	0.0	2.8	3.12	0.36	0.00011	2.82	3.10	0.44	0.03	6.28	6.39	-0.11
RN-20	0.8	2.2	2.92	0.36	0.00032	2.70	3.13	0.41	0.03	6.28	6.27	0.01
RN-21	0.8	2.4	2.92	0.28	0.00016	2.80	3.10	0.41	0.02	6.40	6.33	0.07
RN-22	0.6	2.4	2.96	0.30	0.00003	2.88	3.01	0.39	0.03	6.26	6.31	-0.05
RN-23	0.4	2.8	2.73	0.30	0.00022	2.64	3.20	0.38	0.01	6.23	6.23	0.00
RN-24	0.4	2.4	3.04	0.28	0.00022	2.60	3.01	0.35	0.03	6.12	5.99	0.13
PRT-1	0.6	3.2	3.75	0.32	0.00032	3.68	3.90	0.36	0.05	7.87	7.99	-0.12
PRT-2	0.6	2.8	4.79	0.40	0.00011	4.04	4.12	0.50	0.05	8.59	8.71	-0.12
PRT-3	1.0	2.6	4.17	0.40	0.00027	2.76	3.77	0.53	0.05	8.17	7.11	1.06

equivalent ratio of dissolved Ca:HCO₃ in the waters resulting from calcite weathering is 1:2, whereas for dolomite weathering it is 1:4. If sulphuric acid is the

weathering agent, then the Ca:SO₄ ratio in the waters would be 1:1 for calcite and 1:2 for dolomite. In Renuka waters the Ca:SO₄ ratio is almost 1:1, indicating a possi-

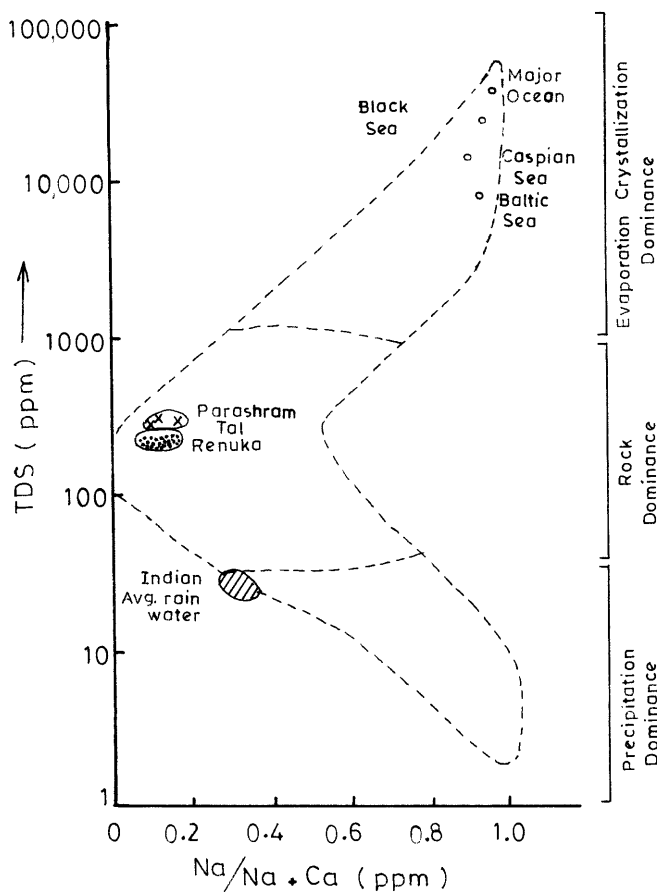
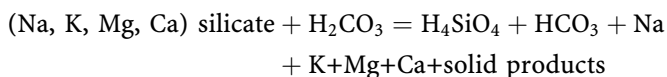


Fig. 3

Plot of Renuka Lake data on Gibbs (1970) diagram depicting dominant factors responsible for the ion chemistry. *Dot* Renuka Lake; *cross* Parashram Tal water chemistry

bility that sulphuric acid formed because the oxidation of reduced sulphur replaces carbonic acid as a source of protons for rock weathering [see Eqs. (3) and (4); Stallard and Edmond 1983].

The solution products of silicate weathering are more difficult to quantify because the degradation of silicates is incongruent, generating a variety of solid phases (mostly clays) along with dissolved species. A general reaction for weathering of silicate rocks with carbonic acid can be written:



The quantities of cations and anions released to solution are determined by the proton source, composition of parent rock and the solid products of the chemical weathering.

In Renuka Lake, calcium and magnesium are the major cations, together accounting for 83–95% of the cations (Table 3, Fig. 4a, b). Among the anions, bicarbonate and sulphate are dominant and are almost in the same proportion; the former accounts for 37–51% and the later for 45–52%, whereas chloride is <6%. The contribution of (Na + K) is between 4 and 7% of the major ion budget of the

lake. The silica concentration ranges between 90 and 120 μmol^{-1} . Figure 5 is a plot of (Ca + Mg) vs HCO_3 in which points lie much above the equiline and are scattered depicting that HCO_3 is deficient to (Ca + Mg), which requires (SO₄ + Cl) to balance the charge. This is demonstrated by Fig. 6, which shows the charge balance between (Ca + Mg) and alkalinity + SO₄; most of the data points closely approach the 1:1 trend. The tendency for data to fall below the 1:1 trend reflects the requirement that a portion of the anions balances Na + K produced by the weathering of silicate rocks. In a triangular plot of SiO₂, (SO₄ + Cl) and HCO₃ (Fig. 7), the samples plot along HCO₃–(SO₄ + Cl) join towards the SO₄–Cl apex, indicating high concentrations of (SO₄ + Cl); particularly the former derived from black shales/gypsum. The average (Ca + Mg)/HCO₃ equivalent ratio of ± 2.55 suggests carbonate dissolution. However, the (Ca + Mg)/T_z+ ratio is 0.97 and if silicate weathering is considered to be the primary source of (Ca + Mg), it would require the terrain to be dominated by alkaline-earth silicates. However, this is not reflected in the regional geology of the catchment. Therefore, the abundance of (Ca + Mg) in the lake can be attributed to carbonate weathering, which is consistent with the carbonate lithology in the area and also to some extent from groundwater. The (Ca + Mg) vs T_z+ plot (Fig. 4a) of lake waters have a linear spread a little below the 1:1 line, indicating that (Ca + Mg) accounts for most of the cations with some contribution of alkali to the major ions of the lake, which may be derived from silicate weathering because silicate rocks outcrop in the region. The plot of (Na + K) vs T_z+ indicates that the data are grossly deficient in alkalis and (Ca + Mg) accounts for most of the cations in the lake. In these waters, the (Na + K)/T_z+ ranges between 0.04 and 0.08 (mean = 0.05) (Fig. 4b). The relatively low ratio leads us to infer that the contribution of cations via silicate weathering is insignificant in this lake.

Clay mineralogy of lake sediments and silicate weathering in the basin

The evaluation of silicate weathering from water chemistry is a difficult exercise as many silicate weathering reactions occur simultaneously. However, the dissolved silica derived uniquely from the weathering of silicates, sodium, potassium and the data on the mineralogy of sediments can be utilised for the assessment.

The clay mineral composition of the sediments collected from the basement (grab samples) and cores is ~1–1.5 m in length and is dominated by illite (52–93%), chlorite (7–48%) and kaolinite–chlorite mixed layer silicates of between 1 and 2%. Non-clay minerals are calcite, dolomite and quartz. The Chemical Index of Alteration (CIA) values of core fraction of sediments ranges between 62 and 82 with decreasing depth, with an average of 76, whereas CIA values of average shales is reported to be between 70 and 75. This indicates fairly strong weathering in the catch-

Table 3
Percentage of equivalent per million of constituent in Renuka Lake

Location No.	Cations			Anions		
	Ca	Mg	(Na + K)	SO ₄	Cl	(CO ₃ + HCO ₃)
RN-1	38.57	44.71	16.71	45.55	17.48	36.97
RN-2	45.15	48.74	6.13	49.06	3.77	47.17
RN-3	39.64	54.10	6.25	46.71	4.84	48.44
RN-4	39.79	54.16	6.05	46.71	4.84	48.44
RN-5	48.39	45.80	5.80	48.76	4.94	46.30
RN-6	48.11	46.38	5.51	51.91	4.11	43.99
RN-7	45.97	48.45	5.57	51.63	4.96	43.41
RN-8	48.61	45.99	5.71	55.93	4.52	39.55
RN-9	44.39	49.68	5.93	46.19	5.19	48.62
RN-10	41.38	52.24	6.83	43.25	4.84	51.90
RN-11	46.26	48.44	5.29	49.54	4.31	46.15
RN-12	44.70	50.15	5.14	48.44	4.97	46.58
RN-13	46.03	49.21	4.76	49.92	5.12	44.80
RN-14	45.66	49.07	5.26	51.95	4.37	43.68
RN-15	46.55	48.96	4.49	47.10	4.52	48.38
RN-16	48.93	46.79	4.28	46.79	5.13	48.08
RN-17	43.48	51.61	4.91	47.74	5.40	47.22
RN-18	45.07	48.97	5.97	48.67	4.67	46.67
RN-19	44.13	48.51	7.35	49.68	5.73	44.58
RN-20	43.06	49.92	7.02	46.50	5.73	47.77
RN-21	44.23	48.97	6.79	45.62	4.37	50.00
RN-22	45.64	47.70	6.66	47.28	4.79	47.92
RN-23	42.37	51.36	6.26	43.82	4.81	51.36
RN-24	43.40	50.25	6.34	49.67	4.57	45.75
PRT-1	46.06	48.81	5.13	47.65	4.01	48.28
PRT-2	46.38	47.30	6.31	55.76	4.66	39.58
PRT-3	38.82	53.02	8.16	51.04	4.89	44.06

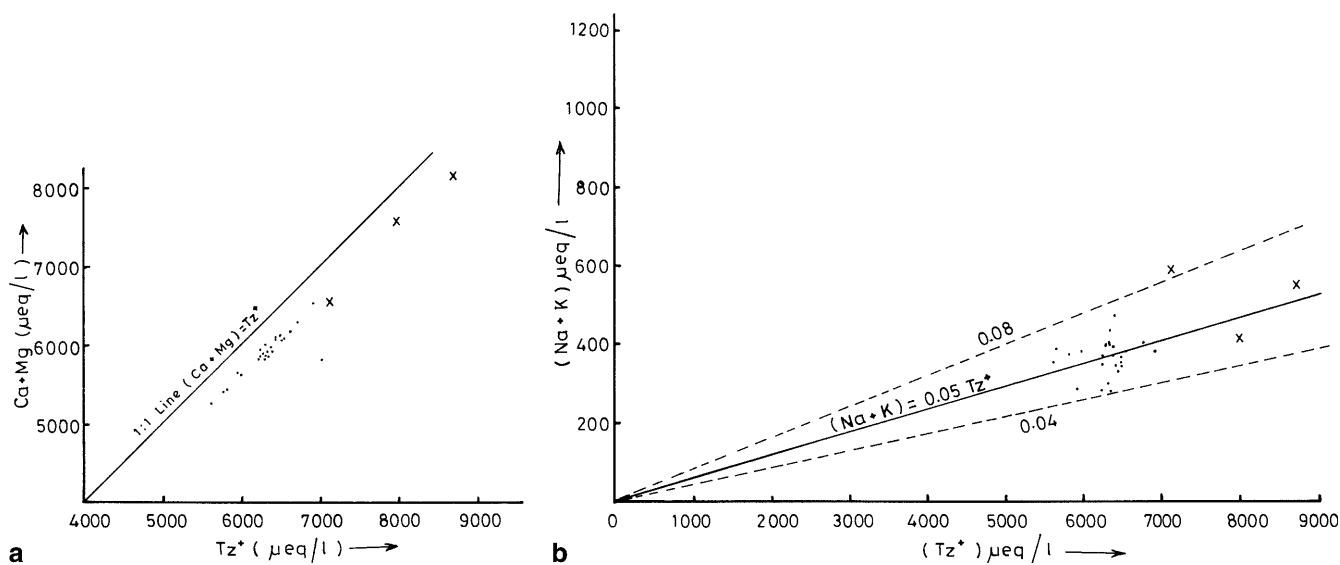


Fig. 4
a Scatter diagram of (Ca + Mg) vs total cations (T_z^+) for Renuka Lake. (Ca + Mg) accounts for most of the cations in the lake and, as the data points fall a little below the 1:1 line, some contribution of alkali is expected. b Scatter diagram of (Na + K) vs (T_z^+), indicating that the data are significantly deficient in alkalis

ment area. The rate of sedimentation of 3.3 mm/year, estimated from Pb²¹⁰ measurement in core samples of Renuka Lake, also reflects a similar environment. The low K₂O and Na₂O in lake water chemistry suggests a greater

resistance to weathering of the former and is used in the generation of clay minerals. The (Na + K)/ T_z^+ ratio is an index to assess the contribution of cations via silicate weathering (Stallard and Edmond 1983, 1987). This ratio on average is 0.058 for Renuka and 0.065 for Parashram Tal. The low (Na + K)/ T_z^+ ratio reflects that there is no significant contribution of cations to the lake waters from the degradation of aluminosilicates. This supports the earlier inference based on (Ca + Mg) abundance and (Ca + Mg):HCO₃ ratio that carbonate weathering is the major source of cations to the lake waters.

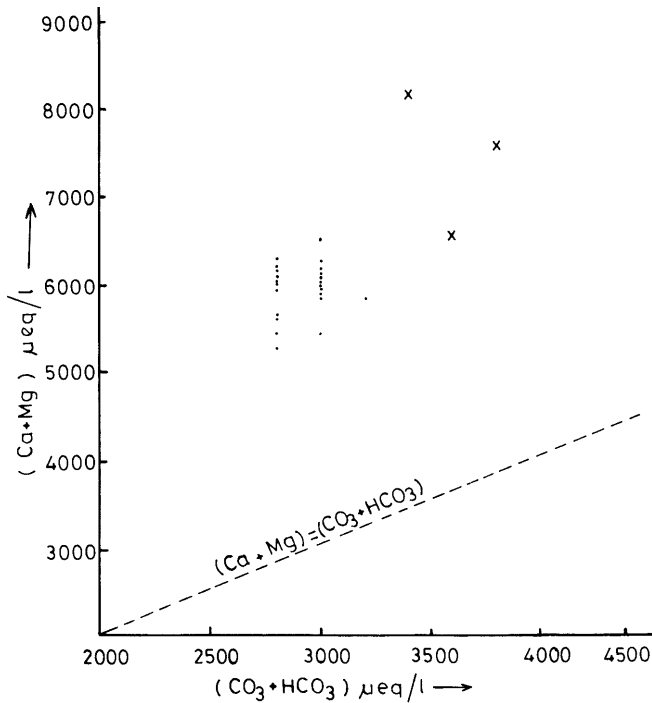


Fig. 5

Scatter diagram of (Ca + Mg) vs (CO₃ + HCO₃) for Renuka Lake. The data plot above the equiline and are scattered, indicating that HCO₃ is deficient in (Ca + Mg), which require (SO₄ + Cl) to balance the charge

The silicate weathering processes have often been interpreted by a Si/(Na + K) ratio. This ratio, which is high in carbonate weathering, is about 0.55 in Renuka waters, probably because of a lower silica content than the alkalis. However, the role of algal productivity on Si concentra-

Fig. 6

Scatter diagram of (Ca + Mg) vs (SO₄ + CO₃ alkalinity). Data plotted close to the 1:1 line and with a tendency to fall below this line indicate that a portion of the anions balances (Na + K)

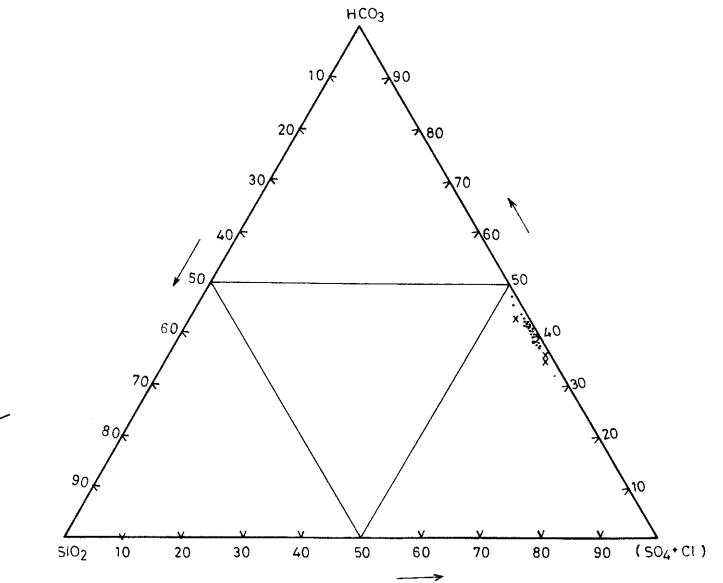
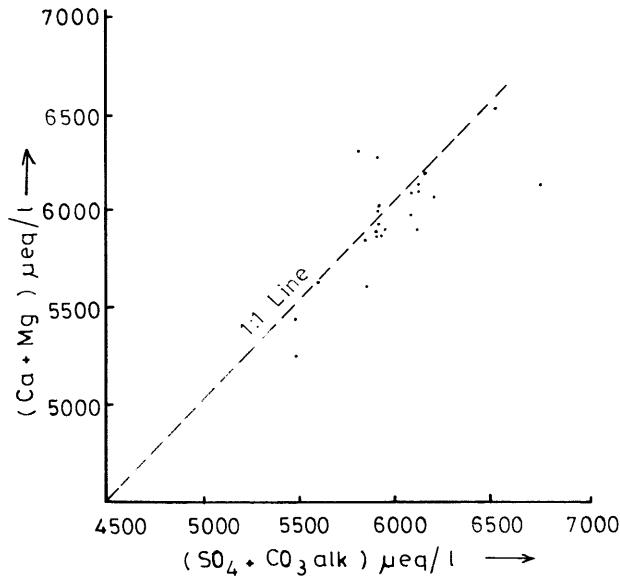


Fig. 7

A triangular plot of SiO₂, (SO₄ + Cl) and HCO₃ of Renuka Lake waters. The points lie along HCO₃-SO₄ + Cl join towards (SO₄ + Cl) apex, indicating a high concentration of sulphate

tions restricts the application of Si/(Na + K) as an index of silicate weathering (Stallard and Edmond 1983; Sarin and others 1989). In a thermodynamic approach to establish the clay mineral assemblages, which would be consistent with the water chemistry, the chemical composition of the lake waters is plotted on a log activity diagram K/H-H₄SiO₄ after Garrels and Christ (1965) and Stallard (1980). Most of the data points fall in the kaolinite field (Fig. 8a) except in Mg/H-H₄SiO₄, where the composition plot is in the chlorite field and is in conformity with the clay minerals (Fig. 8b). In other cases, it is not quite consistent with the clay mineral composition of the sediments, which shows that kaolinite is only a minor constituent. Such an inconsistency between the water chemistry and clay mineral data can arise for various reasons:

1. Lack of proper chemical equilibrium between solution and solid phases.
2. Slight uncertainties in the free energies of the minerals, which could drastically shift the boundaries between the various mineral phases.
3. Non-conservative behaviour of silica in waters resulting from its biological removal.

The computed P_{CO_2} and saturation indices for calcite (SI_c) and dolomite (SI_d) are listed in Table 4. The average P_{CO_2} value -3.2 atm of Renuka water is comparable with the atmospheric P_{CO_2} value of -3.5 (Wigley 1973) and is in equilibrium with calcite, which has an average pH value of 8.43. In contrast, in Parashram Tal, the calcium and bicarbonate concentrations are high and pH is low at 7.91, because the water is in equilibrium with calcite at a higher P_{CO_2} value (-2.68 atm avg.). The higher sulphate, chloride, potassium and sodium contents have been largely derived from human activities, for example, sewage, agricultural wastes, etc., as the inlet Nala opens into the Tal (see Fig. 1; Langmuir 1971).

The plot of saturation index of calcite vs dolomite (Fig. 9), after Stallard and Edmond (1987), demonstrates that Renuka Lake water is supersaturated with respect to both calcite and dolomite, indicating carbonate lithology in the catchment. It is therefore concluded that although both carbonate and silicate lithologies are exposed in the catchment, the former is more susceptible to weathering, and has been the potential source of major ion composition of the lake waters rather than silicate rocks. Further, in core samples, whereas other chemical constituents decrease with depth, Ca increases. This is attributed to limestone lithology at the basement (Mandhalis) and is consistent with the above conclusions.

Conclusions

The Renuka Basin is a unique example of the susceptibility of catchment lithology to the impact of weathering and its contribution to major ion chemistry of waters. This study

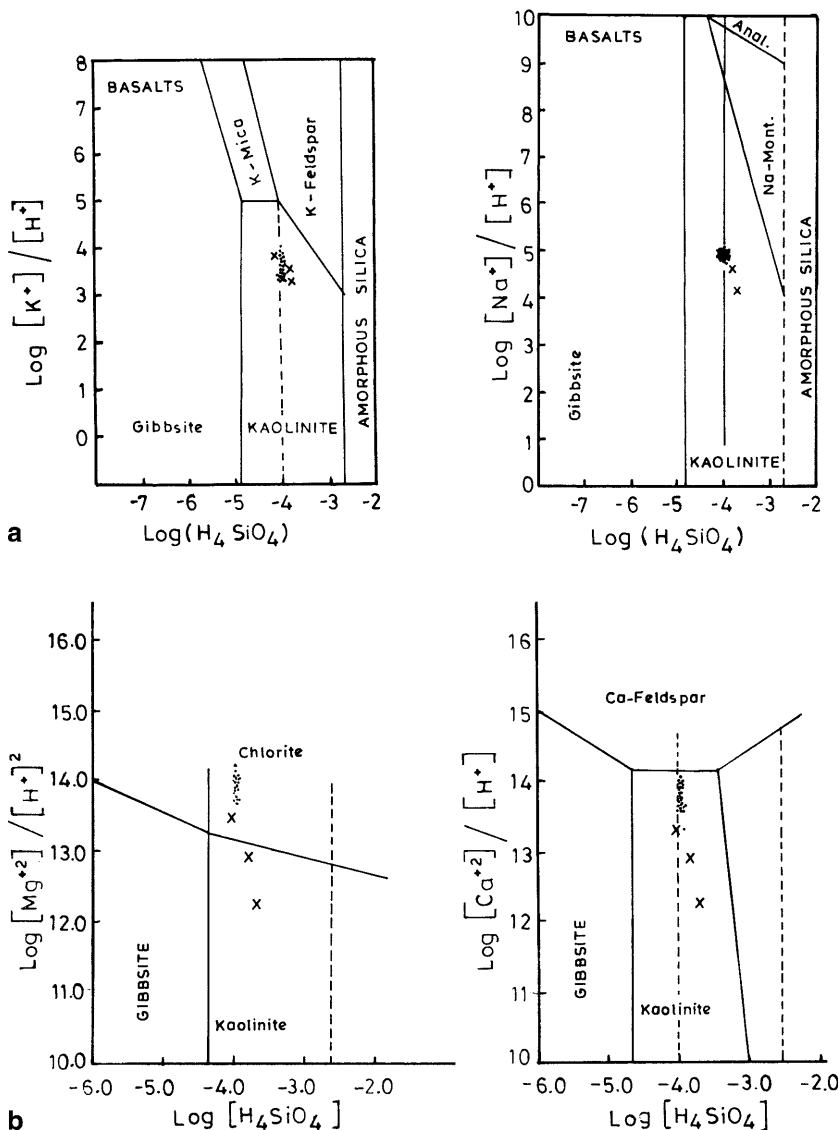


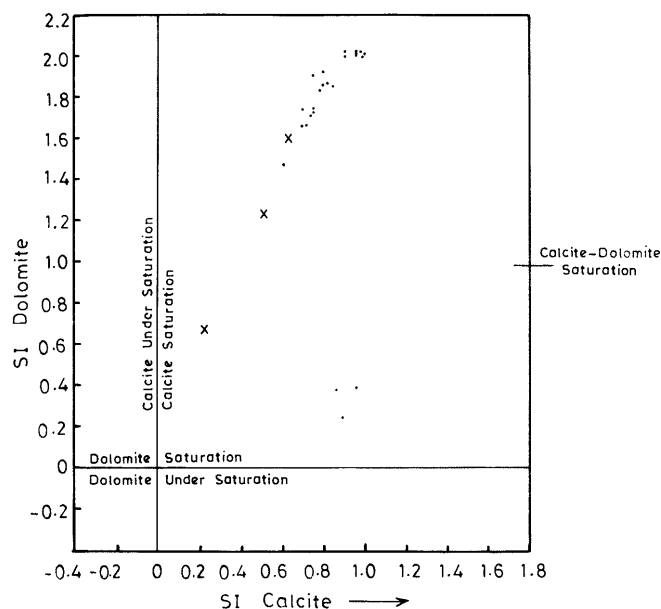
Fig. 8a, b
Stability diagrams for the silicate system (after Garrels and Christ 1965)

Table 4Log P_{CO_2} , S_{lc}, S_{ld}, log aCa²⁺/aMg²⁺ for Renuka Lake

Location No.	Log P_{CO_2}	S _{lc}	S _{ld}	Log aCa ²⁺ / aMg ²⁺
RN-1	-3.24	+0.78	+1.83	-0.07
RN-2	-3.20	+0.91	+2.06	-0.04
RN-3	-3.32	+0.79	+1.92	-0.14
RN-4	-3.22	+0.70	+1.74	-0.14
RN-5	-3.29	+0.96	+2.11	+0.01
RN-6	-3.23	+1.00	+2.16	+0.04
RN-7	-3.31	+0.90	+2.02	-0.02
RN-8	-3.31	+0.99	+2.16	+0.02
RN-9	-2.97	+0.61	+1.47	-0.05
RN-10	-3.16	+0.74	+1.90	-0.22
RN-11	-3.39	+0.98	+2.18	-0.02
RN-12	-3.31	+0.96	+2.17	-0.05
RN-13	-3.16	+0.82	+1.87	-0.03
RN-14	-3.20	+0.78	+0.04	-0.03
RN-15	-3.24	+0.96	+0.40	-0.02
RN-16	-3.22	+0.84	+1.86	+0.02
RN-17	-3.24	+0.69	+1.65	-0.07
RN-18	-3.38	+0.89	+0.25	-0.04
RN-19	-3.07	+0.86	+0.39	-0.04
RN-20	-3.15	+0.70	+1.66	-0.06
RN-21	-3.11	+0.75	+1.75	-0.05
RN-22	-3.10	+0.75	+1.73	-0.03
RN-23	-3.03	+0.79	+1.86	-0.08
RN-24	-3.10	+0.74	+1.72	-0.04
PRT-1	-2.24	+0.22	+0.67	-0.03
PRT-2	-2.62	+0.51	+1.23	-0.01
PRT-3	-2.96	+0.63	+1.59	-0.13

chemistry of waters; however, the susceptibility to weathering of the latter has dominantly controlled it. The water chemistry is (Ca + Mg)- and (HCO₃ + SO₄)-dominated and the role of (Na + K) associated with silicate weathering is not pronounced. The sulphate derived from pyrite-ferrous black shales and gypsum by a process of reduced sulphur replaces alkalinity in the charge balance. The reaction of carbonate to sulphuric acid as a proton source during weathering appears plausible in the basin and accounts for high SO₄ contents in waters. The fairly strong weathering indicated by the CIA value and rate of sedimentation (3.3 mm/year), as obtained by Pb²¹⁰ estimation in core sediment samples, is the primary source of major ion concentration in the lake waters. However, some contributions from other sources, for example groundwater and anthropogenic input, is not ruled out and is reflected in Parashram Tal. The clay mineral composition of sediments is consistent with a shale-slate, sandstone lithology in the catchment area, and low K₂O over Na₂O justifies its greater resistance to weathering and its utilisation in the formation of clay minerals. The saturation index data of calcite and dolomite indicate supersaturation of both and support the existence of carbonate lithology in the catchment area, which primarily controls the water chemistry of the lake.

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**Fig. 9**

Relation between saturation indices of calcite and dolomite (adopted from Stallard and Edmond 1987)

provides significant information on the processes controlling the major ion chemistry of lake waters. The crumpled, shattered, shale-slate, sandstone, quartzite and limestone rocks have contributed to the ion

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