

Artificial ground water recharge and recovery of a highly saline aquifer

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Aquifer storage and recovery (ASR) is an effective method of recharging reclaimed or surplus surface water into confined, or semi-confined permeable formations for later extraction as needed. A key factor in the long-term viability of ASR is the extent of mineral interaction between two dissimilar water types, their recoverable fractions and consequent impact on water quality and aquifer stability. An ASR well study was undertaken in the semi-arid region of northern India to assess the technical viability, environmental sustainability and commercial/economic feasibility of the ASR system in a generic sense. About 2000 m³ of canal water was injected in each recharge cycle aquifer and 100% of the mixture was extracted during each recovery cycle of the experiment. The study revealed that groundwater quality of the recovered water was better than that of the native water and recovery percentage of recharged water (EC ≤ 2 dS m⁻¹) increased from 47% to 74% in successive recovery cycles. The potassium concentration in the recovered water was greater than that of the injected water as a result of potassium release from clay minerals in the aquifer. Borate was also released from the aquifer due the tourmaline dissolution and desorption from clay minerals under lower pH conditions caused by surface water injection.

Keywords: Aquifer storage and recovery, groundwater, hydro-geochemistry, shallow cavity well.

AQUIFER storage and recovery (ASR) is a relatively new water resource management technology, which has been put to a wide range of uses¹, including improvement of groundwater quality for irrigation, particularly in arid, semiarid and coastal areas²⁻⁵. ASR involves subsurface freshwater recharge and subsequent extraction during periods of water deficit or high demand through successive cycles to meet all crop/plantation water requirements. This has not been a part of traditional practices in water resource management because success relies on an emerging understanding of the subsurface processes. However, success of ASR operations depends on the availability of good quality water for recharge and the ability to recover useful quantities of good quality water.

The excess surplus rain, canal and river water available during wet periods may be recharged to improve the quality of native brackish aquifers to increase crop productivity in dry periods.

More than 53% of the groundwater in Haryana state of northern India is brackish (EC > 2 dS m⁻¹), and in other parts of country, this number ranges from 32 to 83% (ref. 6). Out of the total surface water potential of Haryana (14.8 × 10⁹ m³/annum) about 36% goes unutilized⁷. This suggests that other semi-arid regions could also have a similar large potential for utilizing the excess fresh surface water to improve the quality of underground brackish water using the ASR technology.

Most wells in northern India are cavity types and do not clog when recharged with fresh water, even if sediment load is as high as 900 mg l⁻¹ (ref. 5). Clogging has been reported to be the major problem in most of the filter type ASR wells⁸⁻¹¹. Cavity wells are shallow wells installed in aquifers (15–100 m deep), where an empty space or cavity is formed below the impermeable layer¹².

The geochemistry of ASR systems is very complex and is still being studied. Prior knowledge of geochemical reactions occurring in the aquifer during mixing of recharge water with groundwater of different mineral composition and pH, and possible reactions with the mineral assemblage of the host rock would help in the installation, operation and sustaining an ASR system. An understanding of precipitation of iron, manganese and arsenic^{1,13-15} in the aquifer by injecting pH optimized water may be utilized to reduce impact of these elements on drinking water and the clogging of ASR wells. Similarly, the knowledge of enhanced dissolution of calcite minerals in the aquifers can be used to increase the hydraulic conductivity of the aquifer^{10,16,17}.

The present study was, therefore, initiated at the Soil Research Farm of Chaudhary Charan Singh Haryana Agricultural University (CCS HAU) Hisar, Haryana, India with the objectives to quantify (i) the mixing and physicochemical interactions between native and recharged water and (ii) the effect of fresh water recharge on quality improvement of recovered water from cavity type brackish ASR well for irrigation purpose.

The recovery percentage I is defined as the percentage recovered water volume V_r at any recovery time t_r to the recharged volume V_i .

$$I = \left[\frac{\int_{t_{r1}}^{t_{r2}} q_r(t) dt}{\int_{t_{i1}}^{t_{i2}} q_i(t) dt} \right] 100 = \left[\frac{V_r}{V_i} \right] 100, \quad (1)$$

where t_{i1} is the time that recharge starts, t_{i2} time that recharge ends, t_{r1} time that recovery starts, t_{r2} the time that recovery ends, $q_i(t)$ the recovery rate as a function of

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time, $q_i(t)$ the recharge rate as a function of time, V_r the volume recovered between recovery time t_{r1} and t_{r2} and V_i the volume recharged between recharging time t_{i1} and t_{i2} .

The percentage of native water in the cumulative volume of recovered water, for any of the quality parameter, was defined consistent with the definition used in refs 17 and 18.

$$M(t) = \frac{C_{rw}(t) - C_i}{C_n - C_i} \times 100, \quad (2)$$

where, $C_{rw}(t)$ is the average concentration of a given parameters in the cumulative recovered volume of water V_r , C_i and C_n are concentrations of the same parameter in recharged and native water. This concentration $C_{rw}(t)$ in cumulative water volume is indicative of the quality change in recovered water stored in the tank before use and can be estimated as

$$C_{rw}(t) = \frac{\int_{t_{r1}}^{t_{r2}} C_r(t) q_r(t) dt}{\int_{t_{i1}}^{t_{i2}} q_r(t) dt} = \frac{\sum C_r(t) V_r}{\sum V_r}, \quad (3)$$

where C_r is the instantaneous concentration of a given parameter as a function of time t in the instantaneous recovered water sample V_r .

Chloride is a conservative ion not supposed to undergo any precipitation, dissolution, adsorption or ion exchange in the soil water system; therefore, it is used as an indicator ion for quantifying the simple mixing process between native and recharged water. The native water percentage C_x in the cumulative recovered water described in the previous section can also be used to quantify the physical and chemical processes. Let C_x for chloride at a recovery be C_{cl} . If a water quality parameter that shows a C_x value close to C_{cl} value (critical limit assumed is within 10% of C_{cl} value)^{1,2}, then the parameter is considered to have gone through the process of mixing only (no physical and chemical reactions). However, a C_x value beyond the range $C_{cl} \pm 0.1 \times C_{cl}$ means that some other interactions have taken place in addition to simple mixing. Depending on whether concentration of the particular parameter in the native groundwater $C_n(X)$ and the recharged water $C_i(X)$ is more than $1.10 C_{cl}$ or less than $0.9 C_{cl}$, different physical and chemical processes will occur and lead to production or consumption of an ion.

The total amount of salt/parameter (TA) present in the recovered volume of water (V_r) can be estimated as

$$TA(t) = \int_{t_{r1}}^{t_{r2}} C_r(t) q_r(t) dt = V_r \times C_{rw}(t). \quad (4)$$

The amount of salt/parameter due to mixing (MA) is estimated as

$$MA(t) = C_n \left[V_r \frac{C_{cl}}{100} \right] + C_i \left[V_r - V_r \frac{C_{cl}}{100} \right]. \quad (5)$$

The amount of salt/parameter produced/consumed (IA) due to geophysical and chemical interaction is given by the difference of TA and MA.

Bicarbonate (HCO_3^-) exists in equilibrium with carbonic acid (H_2CO_3), which in turn can be converted to carbon dioxide and water.



This means that the direction of reaction would depend upon the pH difference between recharged and native water. The relative amount of carbonic acid and bicarbonate ion will be determined by the pH of the equilibrium solution.

Similarly borate ($H_2BO_3^-$) exists in equilibrium with boric acid (H_3BO_3)



The direction of the reaction depends upon the pH difference between recharged and native water.

Dissolution and precipitation of $CaCO_3$ are common phenomena. The solubility of $CaCO_3$ is affected by different factors such as pH, CO_2 , temperature, organic activity, etc. The effect of pH on the solubility of $CaCO_3$ may be described by the Piper diagram¹⁹

At low pH: $4.5 \leq pH \leq 8.4$:



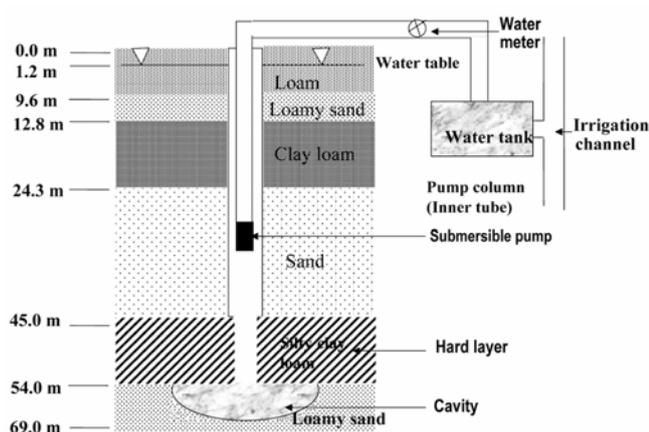
At high pH: $pH > 8.4$:



Unconsolidated materials in the Haryana region of India are very deep (>200 m) and consist of both eolian deposits and alluvial sediments deposited by rivers emanating from the Himalayas. These materials range in comparison from coarse sand to silty, clayey fine sand and are known to contain illite clay²⁰. The underlying bedrock consists of sandstone and limestone down to a depth of roughly 450 m. Groundwater within the unconsolidated deposits occur largely underwater table conditions²¹, and the depth to the groundwater ranges from 1 m to more than 60 m during the pre-monsoon season. Well yields from the shallow alluvial aquifers range between 1.5 and 30 l s⁻¹, and the salinity of the water pumped from these wells

Table 1. Relevant soil physicochemical properties of the Hisar ASR site

Depth (m)	EC (dS m ⁻¹)	pH	Texture	CaCO ₃ (%)	Calcite concretion (%)	Gypsum (%)
0.0–9.6	1.20	8.2	Loam	8.0	32.1	0.014
9.6–12.8	1.19	8.5	Loamy sand	1.1	52.1	0.015
12.8–24.3	0.96	8.6	Clay loam	8.7	0.0	0.020
24.3–45.0	0.76	8.9	Sand	0.4	25.5	0.015
45.0–54.0	0.75	8.4	Silty clay loam	1.0	6.0	0.014
54.0–69.0	0.78	8.6	Loamy sand	4.1	0.0	0.014

**Figure 1.** Schematic diagram of the ASR well.

varies from less than 2 dS m⁻¹ to more than 10 dS m⁻¹. Deeper wells draw from the sandstone and limestone aquifers, which yield up to 150 l s⁻¹.

An ASR site of highly brackish native water was selected at the Soil Research Farm, CCS HAU Hisar, Haryana, India at an elevation of 215 m above mean sea level, where a cavity type well was installed within the shallow, alluvial aquifer. The relevant site characteristics are given in Table 1. The diameters of the inner and outer pipes of the ASR well were 0.075 and 0.275 m (Figure 1). In June 2002, canal water for recharging was available for only two days a week. About 2000 m³ of canal water was recharged by gravity into the cavity type ASR well, employing a siphon system during each cycle to study the effect of a successive number of cycles. Recovery of the same quantity was started immediately after recharge without any storage time.

Sediment samples from different layers taken during the installation of piezometers were oven dried and ground gently with the pestle–mortar. The fraction remaining (concretions) on a 2 mm sieve was analysed for calcite. The sediment passed through the sieve was analysed for different physicochemical properties. Sediment analysis was done with standard methods. The relevant physicochemical properties up to the aquifer are given in Table 1. Samples of recovery water as a function of recovery time and of recharged and native water were analysed for temperature, organic carbon (OC)²², cations

Na⁺, K⁺ (flame photometer), Ca²⁺, Mg²⁺ (versenate method, ethylene diamine tetraacetic acid (EDTA)), NH₄⁺, Zn²⁺ and anions CO₃²⁻, HCO₃⁻ (acidimetric method) Cl⁻ (potassium chromate method) SO₄²⁻ and BO₃⁻ (calorimetric method). Percent error in ionic mass balance E_m was calculated¹ as:

$$E_m (\%) = 100 \left[\frac{\sum (EC_c - EC_a)}{\sum (EC_c + EC_a) / 2} \right], \quad (10)$$

where EC_c and EC_a are cation and anion concentrations in mmolc l⁻¹.

Recharge rates were less than recovery rates due to a shallow groundwater table. Recharge and recovery rates remained fairly constant in each cycle at an average value of 23.23 m³ h⁻¹ and 60.21 m³ h⁻¹, respectively. Clogging was not observed at the site, as recovery rates remained unaffected with successive ASR cycles despite the sediment load of 200 mg l⁻¹ in the recharge water.

Cationic and anionic composition, and EC and pH of recharged water, native groundwater and recovered water along with the average concentration (C_{rw}) at 100% recovery and the corresponding mixing percentage C_x are presented in Table 2. Less than 10% error in charge balance E_m (eq. (10), Table 2) validated that the laboratory analyses for meaningful interpretation of aquifer geophysicochemical interactions.

As chloride does not participate in geophysical interactions¹, it was used as an indicator ion for quantifying the mixing process between native and recharged water. The chloride concentration C_{cl} in the cumulative recovered water volume at any recovery percentages I quantifies the simple mixing process as the fraction of native water mixed in the recovered water. Simple mixing as represented by chloride in native water percentage in the recovered water at 100% recovery C_{cl} decreased linearly with successive cycles as:

$$C_{cl} = -1.58 SC + 21.95, \quad r^2 = 0.99, \quad (11)$$

SC is the Successive ASR cycles from 1st to 4th.

This was because recharged water left in the aquifer after each cycle acted as a buffer zone that restricted direct mixing of recharged water with native water, and

Table 2. Concentration (mmol l⁻¹) of different quality parameters in native (C_n), injected (C_i) and cumulative recovered water (C_{rw}) at 100% recovery

Parameter	C _n	C _i	C _{rw} (C _x)			
			1st	2nd	3rd	4th
EC (dS m ⁻¹)	28.4	0.46	6.15 (20.1)	8.4 (28.1)	7.3 (24.3)	7.0 (23.5)
Cl ⁻ (mmol l ⁻¹)	261	1.0	54.3 (20.5)	49.3 (18.6)	45.8 (17.2)	41.7 (15.7)
SO ₄ ²⁻ (mmol l ⁻¹)	3.90	0.16	0.5 (11.0)	0.5 (9.9)	0.4 (7.8)	0.3 (4.8)
HCO ₃ ⁻ (mmol l ⁻¹)	24	0.60	11.17 (45.18)	9.9 (39.96)	9.1 (36.54)	8.5 (33.73)
BO ₃ ²⁻ (mmol l ⁻¹)	0.30	0.005	0.18 (53.0)	0.14 (42.6)	0.13 (37.7)	0.12 (36.5)
Na ⁺ (mmol l ⁻¹)	159.1	0.49	27.17 (16.92)	38.11 (23.80)	35.76 (22.32)	34.08 (21.00)
K ⁺ (mmol l ⁻¹)	2.11	0.16	1.28 (57.51)	1.13 (49.96)	1.06 (46.41)	0.93 (39.41)
Ca ²⁺ (mmol l ⁻¹)	19.5	0.60	7.45 (36.22)	7.03 (34.02)	5.96 (28.35)	5.87 (27.91)
Mg ²⁺ (mmol l ⁻¹)	48	0.40	15.02 (24.32)	11.04 (22.97)	10.94 (21.74)	9.14 (20.51)
Em (%)	9.80	4.22	-6.40	-7.32	-5.40	-3.68
pH	8.45	7.65	8.20	8.10	8.07	8.09

Figures in parenthesis is the mixing percentage of native water at 100% recovery.

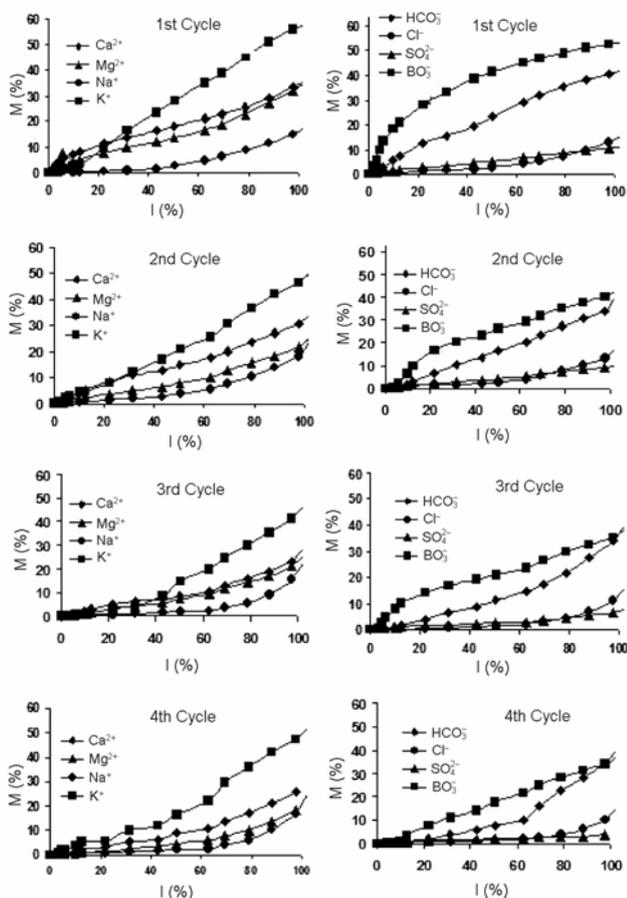


Figure 2. Amount of quality parameters recovered with time in the recovered water in all the ASR cycles.

this led to successive decreases in the proportion of native water in the recovered water with successive cycles.

A comparison of each parameter of chloride in the native water percentages in the recovered water at 100%

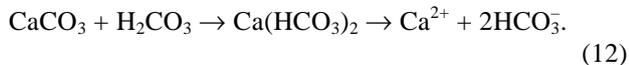
recovery showed that calcium, bicarbonate, borate and potassium have been most affected by geochemical reactions between the native groundwater and recharged water (Table 2) Other parameters in the recovery water were mainly affected by simple mixing between native groundwater and recharged water.

The mixing showed an increase in mixing (*M*) recovery percentage (*I*) for all quality parameters for all ASR cycles in Figure 2. This means that the water recovered was a mixture of recharged water and native groundwater and the proportion of native groundwater increased with the recovery percentage, showing increasing mixing *M* as the recovered water is withdrawn radially away from the ASR well. Mixing curves of *M* versus *I* showed that *M* increased linearly with *I* from 0–60% and increased more sharply at *I* > 60% for all cations. For anions, mixing curves of *M* versus *I* showed a increase in all the ASR cycles, and the increase in BO₃ concentration was very high during the initial recovery in three ASR cycles. Dispersion and regional movement of the recharged water bubble may have increased more sharply with increasing *I* > 60%. The dependence of *M* on these factors was also emphasized in ref. 16.

The natural groundwater chemistry is dominated by sodium and chloride. Native groundwater salinity is approximately 18176 mg l⁻¹ (EC = 28.4 dS m⁻¹) and therefore unsuitable for irrigation. Equilibrium with the limestone aquifer leads to significant concentrations of calcium and bicarbonate.

At 100% recovery, percentages of Ca²⁺ and HCO₃⁻ in the cumulative recovered water volume were much higher than that of the simple mixing C_{cl} value with all ASR cycles. This means that if only simple mixing had occurred, the concentration of Ca²⁺ and HCO₃⁻ in recovered water would have been within ±10% of C_{cl}. Therefore, *M* (Ca²⁺ and HCO₃⁻) > 1.10 C_{cl} and C_n (Ca²⁺ and HCO₃⁻) > C_i (Ca²⁺ and HCO₃⁻) suggesting that calcium-bearing mineral calcite CaCO₃ is dissolving. The relatively

low pH value of the recharged water (pH = 7.65) as compared to that of native groundwater (pH = 8.45) may have caused dissolution of calcite (CaCO_3) present in the aquifer material to form Ca^{2+} and HCO_3^-



This means that one mole of calcite mineral (equal to 100 g) would produce one mole of Ca^{2+} and two moles of HCO_3^- . Comparing HCO_3^- production (11679 mol) with Ca^{2+} production (5741 mol) from 2000 m^3 of recovered water during the first ASR cycle, it was found that HCO_3^- and Ca^{2+} were produced almost in a ratio of 2:1 in successive cycles. There is a slight overproduction of HCO_3^- at the study site. Slight overproduction of HCO_3^- as compared to Ca^{2+} was also reported³ and was attributed to a high CO_2 production linked to organic matter oxidation. Hence, dissolution of calcite in equivalent amounts of Ca^{2+} and HCO_3^- was observed in all ASR cycles.

Successive cycles increased the buffer storage volume of recharged water in the aquifer and thus decreased the calcite dissolution and interaction amount IA of Ca^{2+} and HCO_3^- in successive cycles. Nevertheless, their production proportion to their cumulative M also followed the decreasing pattern with successive cycles.

K^+ and BO_3^- concentrations in the recovered water were much higher than the C_{cl} (Table 2). This shows that potassium and borate were released from the aquifer clay minerals, possibly due to freshening of the brackish groundwater. It is likely that potassium was released from the clay minerals such as smectite due to increase in Ca that desorbed Na or from illite, a potassium-bearing mineral from its adsorbed/non-exchangeable state to solution due to increased hydraulic pressure during the recharge process. The relatively low pH of recharge water pH (7.65) as compared to that of native groundwater pH (8.45) may have caused the desorption process in the aquifer and dissolution of borate from tourmaline, a boron-bearing mineral. During the first ASR cycle, 1653 mol (20 kg) of potassium was released in the recovery water. Potassium release decreased with increasing successive cycles, as in case of calcite dissolution. Potassium release decreased from 1653 to 1253 mol in the four successive ASR cycles. Reference 17 also reported potassium release in ASR wells of a semi-arid region.

Groundwater quality of the recovered water in terms of electrical conductivity (EC) was better than that of native water. The proportion of native groundwater in recovered water increased with recovery percentage I . The first water had a much better quality than the water at the end of the season. This would be beneficial for the as they are more sensitive at the earlier stages of growth.

Recovery efficiency is defined as the recovery percentage I at target time to meet the target EC_{rw} of the recove-

red water (2 dS m^{-1}). Recovery efficiency (RE) increased linearly from 47% to 74% with successive ASR cycles.

$$\text{RE} = 9.24 \text{ SC} + 47.32; \quad r^2 = 0.93. \quad (13)$$

Increased RE with successive ASR cycles was due to decreased mixing with increasing buffer storage volume.

The present study showed that all the quality parameters (cation and anion) increased with time in the recovered water in all the ASR cycles. There was a decrease in the simple mixing at 100% recovery C_{cl} with successive ASR cycles, from 20.5 to 15.7. In all the successive ASR cycles the dissolution of calcite was in a ratio of 2:1 of Ca^{2+} and HCO_3^- . Release of Ca^{2+} and HCO_3^- from dissolution of calcite and of K^+ from clay minerals such as smectite and borate due to desorption process at higher pH in the aquifer with successive ASR cycles. With increasing number of ASR cycles recovery efficiency at target EC_{rw} of 2 dS m^{-1} increased linearly from 47% to 74%, showing a buffer volume of good quality water in the aquifer.

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Carbon isotopic evidence for the origin of Himalayan graphite from Almora crystallines

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Graphite is widely associated with the metasedimentary rocks of the Almora Group, predominantly in the Gumalikhet Formation, which were metamorphosed up to the upper amphibolite grade. This graphite occurs in the form of layers, bands, pockets and lenses, hosted within the garnetiferous mica schist and quartzite. The carbon isotope analyses of the representative samples of Almora graphite are presented here. The $\delta^{13}\text{C}$ values range from -23.2% to -31.7% , however with mean value of -29.08% , which attributes that graphite is crystallized from the biogenic carbon during the metamorphism of the host sediments.

Keywords: Almora crystallines, carbon isotopes, graphite, origin of graphite.

ALMORA nappe, the largest among the detached thrust sheets of the crystalline rocks in the Lesser Himalaya, extends from the West of Nayar River to the East of Kali River in Indian Himalaya, and further to the Dandeldhura region in western Nepal. It comprises the allochthonous Precambrian crystalline rocks termed as Almora Group^{1–7}, which from their root zone of the Munsiri Formation, are thrust over the Precambrian–Lower Palaeozoic autochthonous metasedimentary sequence of the Lesser Himalaya. The rocks of the Almora Group are bounded by Almora Thrust which in the North separates them from the underlying metasedimentaries, and in the South forms the contact with low grade rocks of the Ramgarh Group⁷. The extension of this thrust in the western Nepal is designated as Dandeldhura Thrust². Some of the workers considered that the Almora nappe includes both the Ramgarh Group and the overlying Almora Group^{2–4}. The Almora Group comprises granitic and pelitic gneisses, gneissose granite, augen gneisses, granite, mica schists, garnetiferous mica–quartz schists, quartzite and phyllites^{8,9}. The Rb–Sr whole rock age assigned to the granitic gneiss of the Munsiri Formation is $1830 \pm 200 \text{ Ma}$ ¹⁰, and to the gneisses from a similar nappe in Lesser Himalaya is $1865 \pm 50 \text{ Ma}$. The granitic intrusions present in the nappe are about $560 \pm 20 \text{ Ma}$ -old¹¹. A number of workers have studied the geology, structure, petrology and metamorphism of the Almora Group^{3–9}. Valdiya⁷ classified rocks of the Almora Group into three formations, viz.

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