

APPLICATION OF ENVIRONMENTAL ISOTOPES FOR IDENTIFICATION OF POSSIBLE RECHARGE AREAS OF ALLUVIAL SPRINGS OF VISHAW CATCHMENT IN KASHMIR HIMALAYA

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ABSTRACT

Five alluvium controlled springs were selected for hydrogeochemical and isotope study of Vishaw watershed of Kashmir Himalayas, India. Hydrogeochemical study showed that Ca^{2+} , Mg^{2+} and HCO_3^- were the dominant chemical species in water samples. The order of hydrochemical water types identified is $\text{Ca-Mg-HCO}_3 > \text{Ca-HCO}_3 > \text{Na-Mg-HCO}_3$ and hybrid type. Ca-Mg-HCO_3 and Ca-HCO_3 types of spring water resulted from the dissolution of carbonate lithology. Na-Mg-HCO_3 and hybrid water types followed by surface water owes to the interaction of water with multiple lithologies, resulted from weathering of host silicate rocks. The groundwater samples showed a narrow variation in stable isotope content and are clustered above and very close to GMWL, indicating that groundwater has not been greatly fractionated by kinetic evaporation, except Qoimohnag, with $\delta^{18}\text{O}$ value of - 6.9 ‰ which may be due to the mixing of groundwater with recent precipitation. The high deuterium excess of surface and groundwater suggests western disturbances as the source of the recharging precipitation. The mean isotopic values of groundwater were depleted in heavier isotopes than precipitation. The study suggested that the alluvial springs are recharged by the stream of the catchment.

Keywords: Springs, Hydrogeochemistry, isotopes, recharge, Vishaw, Kashmir.

INTRODUCTION

Groundwater is characterized by chemical constituents, isotopes and anthropogenic impurities (Goldscieder and Drew, 2007). The infiltrating waters acquire chemical constituents by various geochemical processes by interaction of water with the host lithology. Dissolved and colloidal solids in groundwater, therefore, provide information about the geology of the recharge areas and environments. Environmental isotopes (δD and $\delta^{18}\text{O}$) on the other hand, are useful for determining the origin of groundwater (Clark and Fritz, 1997). Being a part of water molecule, δD and

$\delta^{18}\text{O}$ are considered ideal tracers for groundwater studies as they are conservative in low temperature and low circulation systems (Clark and Fritz, 1997). These isotopes are used to identify groundwater recharge from streams and other surface water bodies as the isotopic signatures of precipitation and streams are modified by climatic factors like atmospheric temperature and precipitation, by mixing of waters of different signatures and by diffusional exchange with stored water held in the soil pores within the unsaturated zone (Driscoll *et. al.*, 2005).

In this paper isotopic results together with hydrogeochemistry are used to delineate the

recharge sources of the springs of Vishow catchment for better management and protection of these valuable water resources which are used by the local populace for drinking purposes.

STUDY AREA

Location and Climate

Vishow watershed, SE Kashmir, located between 32°20' N and 34°15'N latitudes and 74°30' and 75°35'E longitudes, covers an area of 985 km² (Fig. 1), is dotted with numerous perennial springs. The study area is drained by Vishow stream originating from Kounsemag Lake, a high altitude glacial tarn. The area experiences a temperate climate with average precipitation of 150 mm. There is a great variability of temperature which ranges from 37°C in summers to -15°C in winters (Jeelani, 2005). The Kashmir weather has a marked seasonality and is divided into four seasons; Winter (Nov - Feb), Spring (March - mid May), Summer (mid May - mid Aug) and Autumn (mid Aug - Oct). Winter in the

valley is dominated by Westerlies (western disturbances) originating from the Mediterranean Sea and enters the valley from west or Northwest across the Iranian plateau (Raza, 1978). These depressions are the chief bearers of winter snow and rains in the valley. The frequency of western depressions is equally high during spring but declines substantially as summer advances. Spring season particularly March receives the maximum rainfall of the year and autumn season particularly September receives the minimum rainfall.

Geology and Hydrogeology

The study area has a diverse rock type ranging in age from Paleozoic sedimentaries to recent alluvium (GSI, 1977; Wadia, 1975; Middlemiss, 1910). Upper Paleozoic rocks, lava, pyroclasts and arenites are only marginal to study area, although they support most of the head water drainage. Overlying these is a sequence of Triassic Limestone, though nowhere fully exposed, are almost certainly

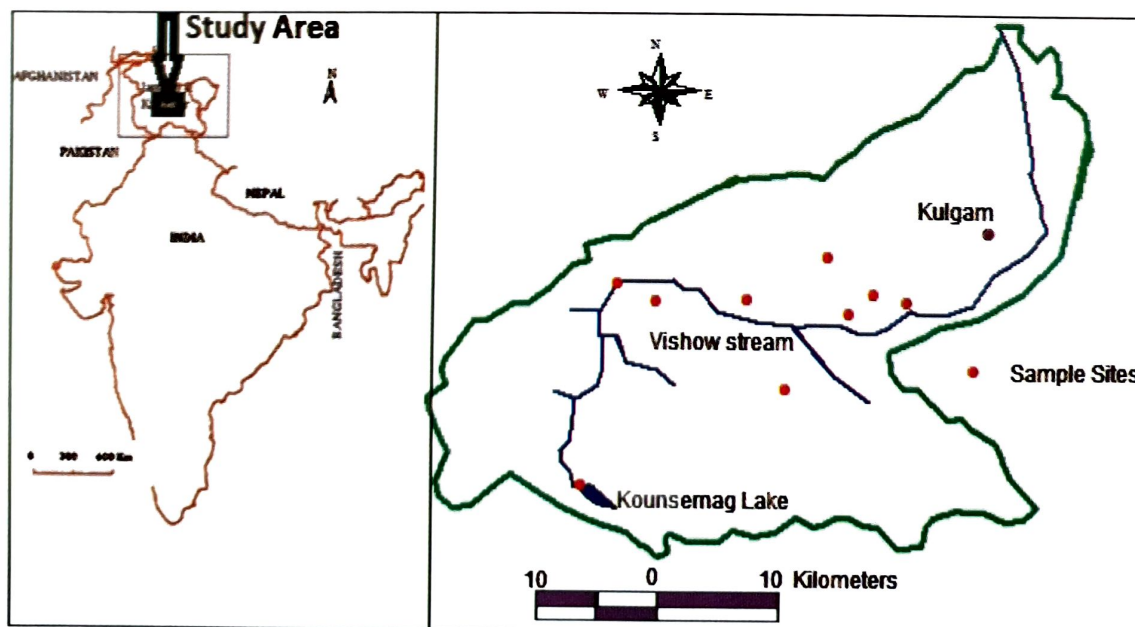


Fig.1. Location map of the study area with sampling sites.

more than 1000m thick (Wadia, 1975), are the dominant geological formations of hydrological importance. Karewas are the fluviolacustrine deposits and contains unconsolidated material like light grey sands, dark grey clays, coarse to fine grained sand, gravel, marl, silt, varved clays, brown loam, lignites etc (Bhat; 1989). The alluvial deposits represent recent sediments contains fine silt and mud, though active flood plains are mainly of coarse gravel and boulders (Jeelani, 2004). The Alluvium and Karewas are well connected with the Triassic Limestone aquifer and Panjal Trap aquifer respectively, which blocks the groundwater flow. The blocking effect leads to the existence of a low but stable and continuous recharge to the alluvium and Karewas aquifer.

MATERIALS AND METHODS

A total of 10 water samples were collected from precipitation, surface water and spring water of Vishav watershed (Fig 1) were collected and analyzed for environmental isotopes and Hydrogeochemistry. Master variables; water temperature, electrical conductivity (EC) and pH were measured insitu using portable water analysis kit. For major ion analysis, samples were filtered through 0.45µm nucleopore membrane filters. All the major ions were analyzed employing standard methods (APHA, 1996). Ca^{2+} and Mg^{2+} were analyzed titrimetrically using standard EDTA. Na^+ and K^+ were determined by flame photometry. HCO_3^- and CO_3^{2-} were determined by standard HCl titration and Cl^- was estimated using standard AgNO_3 titration. SO_4^{2-} and NO_3^- were determined by spectrometer (EI, 1371, UV, VIS).

Stable isotopes, ^2H and ^{18}O were analyzed using IR-Mass Spectrometer (Geo 20-20, Europa) at Isotope Application Division (Bhaba Atomic Research Centre) Mumbai, by equilibration method (Epstein and Mayeda, 1953). For $\delta^2\text{H}$ analysis, 1ml of the water sample was equilibrated with H_2 along with Pt. catalysts at 50°C for 1 hour and the gas was introduced into mass spectrometer. For $\delta^{18}\text{O}$, 1ml of water sample was equilibrated with CO_2 at 50°C for 8 hours and the equilibrated gas was introduced into the spectrometer. The results are reported as δ (delta) values (Craig, 1961) representing per mil deviation from the V-SMOW standard (Vienna Standard Mean Ocean Water) (Gonfiantini, 1981) by the following equation:

$$\delta (\text{‰}) = [(R_{\text{Sample}} / R_{\text{VSMOW}}) - 1] * 10^3$$

Where R refers to $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ ratios. The precision of the measurement for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ was $\pm 1\text{‰}$ and $\pm 0.1\text{‰}$, respectively.

RESULT AND DISCUSSION

Hydrogeochemistry

Chemical analysis of precipitation collected at two locations (Fig 1) demonstrates a narrow range of salinity (TDS; 41-50 mg/l; Table 1). Some parameters like Ca^{2+} , HCO_3^- and SO_4^{2-} show high concentration. This may be attributed to the high altitude and also the regional bedrock in the study area is carbonates.

The surface water samples of Vishav River were collected at two locations. The lowest value of TDS in surface water was recorded high mountain lake (19.2 mg/l) and the highest in stream water (64 mg/l). The pH value ranges from (9.8-9.9), indicated

alkaline characteristics. From the head waters (Kounsarnag lake (3000 m amsl, site L3) to plains at Vishav Stream (2204 m asl), the surface water chemistry exhibits a chemical evolution as shown by Piper trilinear diagram (Fig. 2). As the water moves and infiltrates down gradient, more and

more chemical constituents are added and the water modifies and evolves to different water types depending upon its flow path and the host lithology. The surface water at site L3 had a TDS less than 20 mg/l and the TDS concentration at S4 reached at 50 mg/l.

Table 1. Hydrochemical data of springs, precipitation and surface water collected during September 2007 from Vishoaw catchment

Sample ID	Altitude (m amsl)	pH	Temp. (°C)	EC (µS/cm)	TDS (mg/L)	Hardness (mg/L)	Ca ⁺⁺ (mg/L)	Mg ⁺⁺ (mg/L)	Cl ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)
P1	2435	8.6	11.8	78	50	18	5.61	0.97	1.24	16	0.2	0.01	4.8	0.6
L3	4000	9.8	10	30	19.2	60	4	12.15	10.72	50	9.2	2.3	5.5	2.2
S4	2204	9.9	9	100	64	32	8.81	2.43	6.73	90	10.8	2.6	4.3	5.1
Sp5	1756	9	15	100	64	50	13.62	3.88	4.24	80	6.0	0.7	12.3	5.42
Sp6	1767	9.2	14	90	57.6	44	13.62	2.43	4.24	80	5.7	0.9	21	6.1
Sp7	1738	7.1	13	80	51.2	50	12.8	4.37	2.24	80	5.8	1.1	3.2	9.2
Sp8	1760	8.6	15	160	102.4	72	19.23	5.83	4.74	90	7.1	1.5	8.5	7.7
Sp9	1708	8.5	14	200	128	84	22.44	6.8	5.23	110	6.4	1.6	15.4	7.6
Sp10	1613	8.4	14	150	96	70	19.23	6.8	5.23	110	6	1.5	12.8	6.26

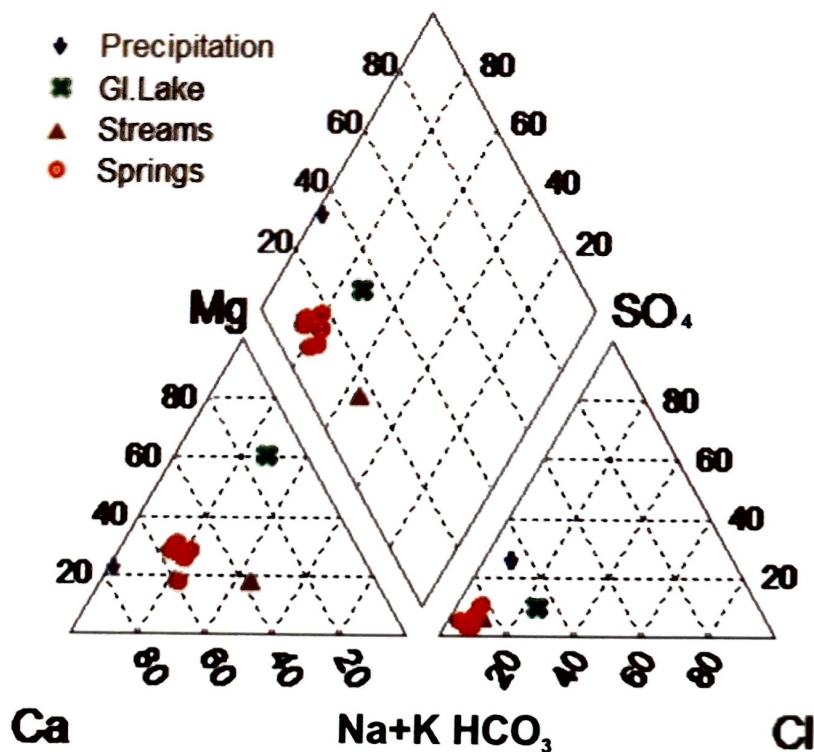


Fig. 2 Piper trilinear diagram showing different water types.

The precipitation increases with increasing elevation and the greater precipitation lowers the TDS of runoff waters. Therefore, these parameters clearly exhibit an altitudinal gradation. Furthermore, meteorological and hydrological conditions significantly influence water chemistry. At lower altitudes temperatures are higher exacerbating the chemical weathering of rocks, increasing the TDS in water and shifting the water chemistry from Ca-HCO₃ to other types.

The hydrochemical properties of groundwater samples collected from the quaternary aquifer system are shown in table 1. The pH of the groundwater ranges from 7.1 to 9.2 with an average of 8.5 indicating an alkaline nature. Total Hardness reflects the trend in the concentration of Ca²⁺ and Mg²⁺, with an average value of 61.6 mg/l. Electrical conductivity averages about 130 μs/cm, indicating low salinity and the corresponding values of total dissolved solids (TDS) estimated from the specific electric conductance values using a multiplication factor of 0.64, show an average value of 83.2 mg/l. Ca²⁺, Mg²⁺ and HCO₃⁻ occur in higher concentrations compared to those of Na⁺, K⁺, Cl⁻ and SO₄²⁻. Average concentration of Ca²⁺ and Mg²⁺ are 16.8 and 5.02 mg/l, while those of Na⁺ and K⁺ are 4.2 and 1.9 mg/l respectively. These cations are possibly derived from chemical weathering of feldspars, mica and other related minerals constituting the basement rocks in the area. HCO₃⁻ is the dominant anion, with an average concentration of 91.6 mg/l, the source of which may be attributed to CO₂ charged recharge. While SO₄²⁻, Cl⁻ and NO₃⁻ have average concentration of 4.3, 4.5 and 7.0 mg/l respectively.

Isotopic Approach

The analyzed stable isotopes of water samples show a great variation (Table 2), being depleted in streams, Glacial Lake, springs and enriched in precipitation. The δ¹⁸O of precipitation samples collected at two station, ranged from -0.11 to -4.22 ‰ with an average value of -2.2 ‰ and from -9.9 to -18.8 ‰ with an average value of -4.4 ‰ for δD. For surface water samples (lake and stream), δ¹⁸O ranged from -8.77 to -8.87 ‰ and from -52.82 to -83 ‰ for δ²H, averaging at -8.2 ‰ and -52.9 ‰. The springs showed a narrow range of stable isotopes, ranged from -6.88 to -8.66 ‰ for δ¹⁸O and -39.99 to -52.05 ‰ for δ²H, at an average of -8.2 and -49.4 ‰. The deuterium excess value d (d = δ²H - 8 δ¹⁸O, Dansgarrrd 1964) for the water samples ranged from 10 to 17.96 ‰. A significant difference in the behavior of deuterium excess in precipitation, surface and groundwater has been observed (Table 2). The surface and groundwater samples has very high deuterium excess (mean = 16.5 ‰), as compared to the deuterium excess of precipitation samples (mean = 12.9).

A part from ionic input from precipitation (recharge), chemical weathering and dissolution of minerals within a geological formation through which water moves determines the water chemistry. The relationship between recharge and discharge may be simple or may be rendered complex such as mixing of unlike waters, interconnected aquifers of different composition, chemical reactions and biological influence. However, the major ion chemistry of groundwater is a powerful tool for determining solute sources and for describing water evolution as a result of

rock-water interaction leading to dissolution of carbonate minerals, silicate weathering and ion exchange process.

Attempted characterization of groundwater in study area using piper diagrams show that the overall chemical character fall with in the alkaline earth water group, indicating predominantly a Ca-Mg-HCO₃ water type. Generally, within the evolutionary trend, groundwater tends to acquire a chemical composition similar to that of sea water (Driscoll, 1986). The occurrence of Ca-Mg-HCO₃ in the study area resulted from dissolution of carbonate hosted lithology. To further examine the effect of lithological weathering, water samples of Vishow watershed were plotted between silicate and carbonate end members (Fig. 3). The results indicate Ca-Mg-HCO₃, Ca-HCO₃ of spring water resulted from the dissolution of carbonate lithology. Na-Mg-HCO₃ and hybrid water types

followed by surface water owed to the interaction of water with multiple lithologies, resulted from weathering of host silicate rocks.

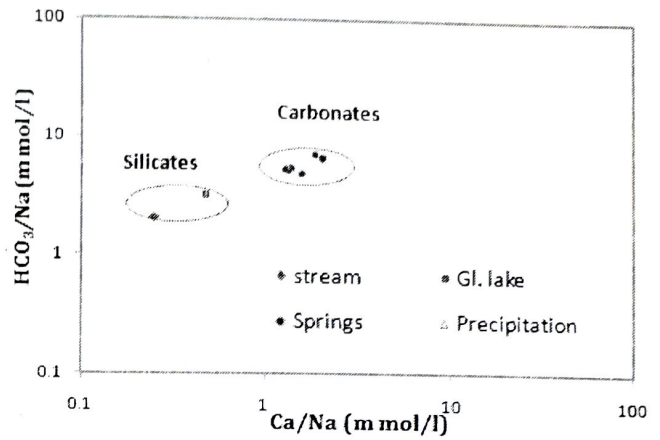


Fig. 3. Major ion chemistry of water samples between silicate and carbonate end members, with spring water samples showing a mixing trend.

On a global average, the general relation between δ²H and δ¹⁸O for natural waters is found to be linear, is defined as Global meteoric water line (GMWL), expressed by the equation (Craig; 1961):

$$\delta^2H = 8 \delta^{18}O + 10$$

Table 2. Isotope data of water samples of the study area.

Sample ID	Location	Latitude	Longitude	Altitude (m amsl)	¹⁸ O (‰)	δ ² H (‰)	d-Excess (‰)
P1	Aru rainwater	- - -	75° 15' 838"	2435	-0.11	9.96	10.84
P2	Aharbal rainwater	33° 38' 482"	74° 47' 322"	2173	-4.22	-18.79	14.97
L3	Kounsarnag lake	33° 26' 372"	74° 58' 232"	4318	-8.77	-52.82	17.34
S4	Vishow stream	33° 39' 647"	74° 47' 140"	2204	-8.87	-53	17.96
Sp5	Kulgamnag	33° 38' 611"	75° 00' 901"	1756	-8.58	-51.95	16.69
Sp6	Chewalgamnag	33° 38' 842"	75° 59' 325"	1767	-8.66	-52.05	17.23
Sp7	Khasarnag	33° 39' 467"	74° 58' 979"	1738	-8.24	-51.9	14.02
Sp8	Shardanag	33° 41' 174"	74° 58' 922"	1760	-8.43	-51.12	16.32
Sp9	Parigamnag	33° 41' 905"	75° 00' 479"	1708	-8.42	-49.68	17.68
Sp10	Koimohnag	33° 43' 079"	75° 04' 866"	1613	-6.88	-39.99	15.05

$\delta^2\text{H}$ values of water samples are plotted against corresponding $\delta^{18}\text{O}$ values as shown in Fig. 4. The meteoric relationship in local precipitation has not been fully determined for the study area. Therefore, the global meteoric water line (Craig, 1961) is shown for reference in Fig. 4. The groundwater samples showed a narrow variation in stable isotope content and are clustered above and very close to GMWL indicates; firstly, the common origin for groundwater and secondly the groundwater has not been greatly fractionated by kinetic evaporation. The mean $\delta^{18}\text{O}$ composition of springs is -8.5‰ , which is close to the mean value of Surface water except koimohnag, with $\delta^{18}\text{O}$ value of -6.88‰ which may be due to the mixing of groundwater with precipitation.

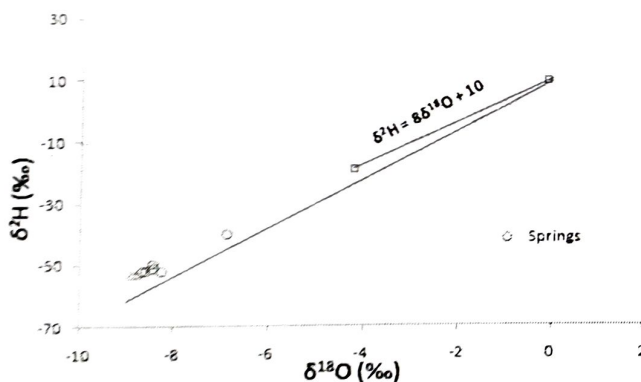


Fig. 5. Relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water samples of Vishav watershed.

In Vishav watershed the oxygen isotope composition of the precipitation decreases with increase in altitude which is consistent with the well known altitude effects (Dansgaard, 1964). Keeping in view the significance of isotope gradients in delineating the recharge areas of aquifers (Longinelli and Selmo, 2003), $\delta^{18}\text{O}$ gradients have been calculated. A mean altitude effect of -0.5‰ per 100m change in elevation has

been calculated in earlier studies (Jeelani et. al, 2010) based on mean precipitation isotopic composition data. The altitude effect however, varied temporally depending upon the source, amount and trajectory of the air mass bringing the precipitation. The altitude effect, however, varied seasonally being lowest in November and highest in March.

The mean isotopic values of groundwater are lower by $> 6\text{‰}$ compared to that of precipitation of the study area. The closeness of isotopic content of springs with the catchment stream and enriched character of the precipitation inferred that springs are recharged by catchment stream.

SUMMARY AND CONCLUSIONS

Water samples from Vishav watershed were analyzed for hydrogeochemistry and stable isotopes to delineate the water sources of alluvial springs. A total of 10 samples were analyzed included 2 precipitation, 2 surface water and 6 spring water samples. We analyzed dissolved major ions, stable isotopes of hydrogen and oxygen of precipitation, streams and spring water samples collected from the study area during September 2007 (Pre-melting). Following is the summary of observed features.

1. Hydrogeochemical data showed that Ca^{2+} , Mg^{2+} and HCO_3^- were the dominant chemical species in water samples and the concentrations of other chemical species like Na^+ , K^+ , SO_4^{2-} , Cl^- and NO_3^- were very low.
2. The order of hydrochemical water types identified is $\text{Ca-Mg-HCO}_3 > \text{Ca-HCO}_3 > \text{Na-Mg-HCO}_3$ and hybrid type. The results indicate Ca-Mg-HCO_3 , Ca-HCO_3 of spring water resulted from the dissolution of carbonate lithology. Na-

Mg-HCO₃ and hybrid water types followed by surface water owed to the interaction of water with multiple lithologies, resulted from weathering of host silicate rocks.

3. The groundwater samples showed a narrow variation in stable isotope content and are clustered above and very close to GMWL, indicate that groundwater has not been greatly fractionated by kinetic evaporation. The surface and groundwater samples have very high deuterium excess, suggesting western disturbances as the source of these waters.
4. The closeness of isotopic content of springs with the catchment stream and enriched character of the precipitation inferred that springs are recharged by catchment stream.

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