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Implication of Epithermal Mineralization as Proxy for Geothermal Energy Potentiality in Puga, Ladakh UT, India

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Abstract: The present study area, Puga, is located along the inflexion point of Indian and Asian plates comprising of zone of anatectic melting, where thermal activity is attributed to the extensive igneous activity during Upper Cretaceous to late Tertiary age. The area is characterized by geysers, past fumaroles, steaming grounds and mud pools with vast spread of sulfur, carbonates and borax deposits with surface temperature of hot springs of 84°C, which is the boiling point of water at ~ 4500 m above mean sea level. It is the only known geothermal system where rare alkali enrichment in thermal fluids follows the sequence: Cs > Li > Rb. Our study shows for the first-time evidence of lithium containing mica mineral, polylithionite, in the thermal spring deposits. The characteristic Na-Cl composition of thermal waters points to recurrent interactions between high-temperature fluids and the crystalline or volcanic rocks in the ancient reservoir beneath, unequivocally suggesting prevailing partial equilibration conditions with rock-forming minerals in thermal waters. The study also shows occurrence of epithermal minerals like jarosite, thenardite, alunite, tincalconite in the hot spring deposits with reservoir temperature estimated from multiple ion exchange geothermometers of ~250°C. Calculations show that meteoric water circulates at a minimum depth of approximately 1.5 km where it assimilates solutes through magmatic convection and emerge as hot springs. High heat flow and Cs-enrichment in thermal fluids are indications of cooling acid magma chamber at a significant depth which influences heat influx and the formation of epithermal minerals. Therefore, this study presents a state-of-art approach demonstrating that the presence of hydrothermal minerals within surface hot spring deposits can act as a promising indicator for identifying shallow high-temperature zones in the reservoir.

Keywords: Hot Springs, Epithermal Minerals, Polylithionite, Geothermometers, Circulation Depth

1. Introduction

Geothermal energy refers to the heat derived from the Earth's core. It is a renewable energy source that can be harnessed for various purposes, including electricity generation and heating purpose [1, 2]. Unravelling geochemistry of fluids of any geothermal system not only reduces the number of exploratory wells in any geothermal project but also categorizes potential wells based on their long-term reservoir performance for future use [3, 4]. This concordantly reduces the overall project cost of any geothermal pilot plant installation. The occurrence of epithermal mineralization in the deposits surrounding hot springs further amplifies this judgement about the presence of high temperature of any geothermal system at shallow sub-surface [6, 7].

In the Tso Morari region, south of the Indus-Tsangpo Suture Zone (ITSZ), geothermal site Puga is located, where active geothermal springs, geysers, past fumaroles, steaming grounds and mud pools can be seen, along a large expanse of

15 sq. km [7, 8]. Puga geothermal field has attracted attention of researchers and explorers from past five to six decades, since initiation of exploration activities by Geological Survey of India during Puga Multipurpose Project in 1970s, due to its multiple geothermal facies: (a) liquid-vapor biphasic system, (b) high reservoir temperature, (c) signs of epithermal mineralization, (d) using geothermal sites for mineral exploration, (e) potentiality for geothermal power generation etc. [9, 10]. The heat source of the Puga reservoir remains mysterious, sparking ongoing debate. It is suggested to be of magmatic origin, yet it is also evident that the heat arises from terrestrial thermal gradients, the decay of radioactive elements within reservoir rocks, certain exothermic reactions, notably those involving sulfide minerals, as well as the heat generated within fault zones due to friction or tectonic activities, all of which cannot be disregarded [5, 11, 12]. Occurrence of hydrothermal minerals on the surface can serve as an indicator of shallow level high temperature regime in any geothermal system [6−8, 13]. The present study reports how epithermal mineralization can serve as a proxy for geothermal energy potentiality with a case-study in Puga, Ladakh Union Territory, India.

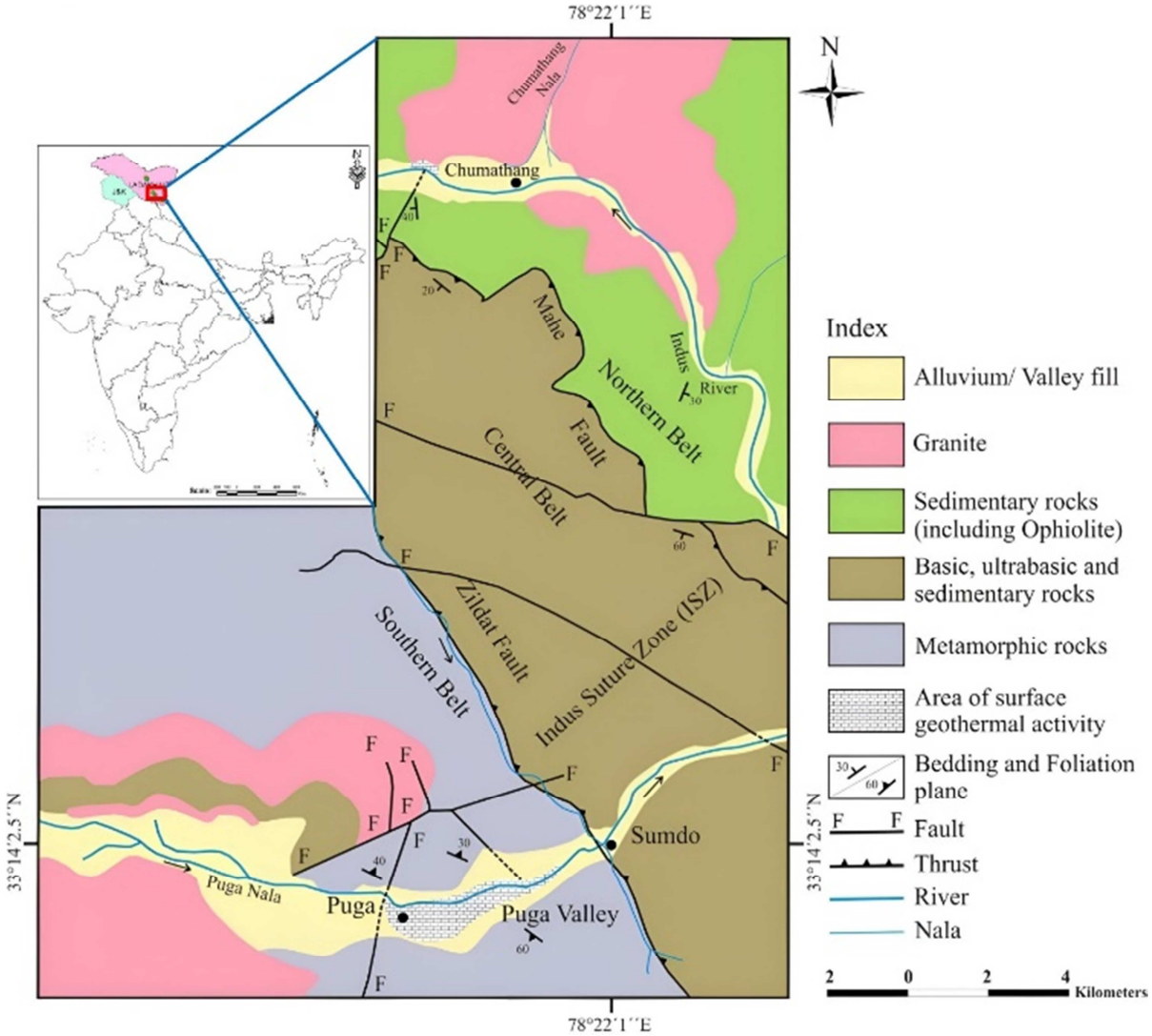

Figure 1. *Location and regional geological map of Puga, study area. [Modified after 5].*

2. Regional Geological Settings

The Puga geothermal field is situated in proximity of southern area of ITSZ, marking the convergence point of the Indian and Asian plates, both of which are significant contributors to the Himalayan orogenic processes [14, 15] Puga, located at an altitude of ~ 4400 m above mean sea level, is known for numerous geothermal springs, sporadically scattered across the entire valley with surface temperature up to 84°C (boiling point of water at that altitude) with splendid manifestations of sulfur and borax deposits [16].

The Puga geothermal manifestation is a part of southern tectonic belt which is actively bounded by several protruding faults: Kiagar Tso fault in the West, Zildat fault in the East, and Mahe fault in the North [11−14]. The Northern tectonic section is comprised of sedimentary rocks belonging to Indus group while in Southern section of the valley, rocks of

Proterozoic age, encompassing paragneiss, schist, quartzite and associated phyllite, limestone and eclogite, which form the base for the fossiliferous Tethyan sediments are exposed still further to the southern section of the valley [8, 17]. Hard reconsolidated hydrothermal breccia is extended upto several depths forming the basement rock of Tso Morari Gneissic Complex (TMGC) which is extended by Polokong La granite in the further west [7, 18] [*Figure 1*].

3. Materials and Methods

Thermal waters collected from the study area, Puga, have maximum temperature of 84°C, which is nearly taken to be the boiling point of water at 4400 m above mean sea level. These waters are collected in three different batches: 500 ml for analysis of major ions, 60 ml for analysis of dissolved SiO_2 which is diluted to 1:10 by distilled water to prevent polymerization and unnecessary precipitation of SiO_2 from thermal waters, and another 60 ml for Hg which is preserved by adding 5% $K_2Cr_2O_7$ and concentrated H_2SO_4. Hot spring deposit and altered rock samples are also collected to investigate evidence of hydrothermal mineralization. Mineral identification in hot spring deposits was conducted utilizing a PANalytical X'Pert Pro powder X-ray diffractometer equipped with a 30mA current and a Cu source, operating at 35 kV. The analysis was performed with the assistance of High Score software, which is enabled with the PDF2 database for accurate mineral identification. The physical parameters like pH, electrical conductivity (EC), total dissolved solids (TDS), and salinity are determined on spot using Hanna water analyzer kit while total alkalinity, total hardness, Ca^{2+} and Mg^{2+} concentrations are also determined on spot using standard alkalimetric and complexometric titrations [4−6, 13, 19]. Other major ions like Na^+, K^+, Li^+, Cl^-, F^-, SO_4^{2-} and 1:10 silica is determined on laboratory using standard analytical procedures with ±5% charge balance error (measurement accuracy). The ions Na^+, K^+, Li^+ are analysed by Systronics 128 Flame Photometer; SiO_2 and SO_4^{2-} are analysed using Thermo (UV330) UV spectrophotometer at absorption maxima of 820 nm and 420 nm using colorimetry and turbidimetric techniques while Cl^- is estimated using argentometric titration procedure. The inductively coupled plasma mass spectrometer (ICPMS) instrument (VARIAN 820 MS) is used for analysis of heavy metals like Cs^+, Rb^+ and other traces present in thermal waters.

Table 1. *Chemistry of thermal discharges in Puga Valley, Ladakh Union Territory, India.*

SAMPLE	Na	K	Ca	Mg	SiO_2	B	Cl	F	SO_4	HCO_3
HS/PU-01	664	76	10	4	143	134	443	12	123	916
HS/PU-02	696	78	24	5	138	134	435	12.8	155	947
HS/PU-03	645	80	4	<2	158	129	444	14.6	119	825
HS/PU-04	512	66	10	4	150	100	405	13	112	623
HS/PU-05	624	72	12	4	126	153	426	13.6	119	866
HS/PU-06	621	65	5	<1	138	119	406	14	112	823
HS/PU-07	656	78	9	9	140	132	429	12.8	128	1056
HS/PU-08	632	73	2	2	143	136	419	11	134	810
HS/PU-09	588	65	22	6	157	110	433	13.5	155	956
HS/PU-10	592	59	12	3	150	129	395	12	149	725

Average concentration of rare alkalis: Li^+ ~ 6.8 mg/l, Rb^+ ~ 0.8 mg/l, Cs^+ ~ 7.7 mg/l

4. Results and Discussions

4.1. Hydrogeochemistry of Thermal Fluids

Thermal fluids of Puga are either relatively dilute Na−Cl type or mixed ion type (transition zone where no pair of cation and anion exceeds 50% of total concentration), with abundance of HCO_3^- and Cl^- ions having total dissolved solids ~2400 mg/L (Figure 2a) [8]. It is a living hydrothermal system with consistent abundance of conservative species in thermal waters like Cl, B, Li, F, and Cs which provide an unambiguous evidence of a single reservoir source of these thermal discharges. Comparing with some global hydrothermal systems, like Steamboat springs of Nevada-USA, Yangbajing of China, El Tatio of northern Chile, the trend of rare alkali enrichment (RAEs) follows the sequence where either Li > Rb > Cs or Rb > Li > Cs. Puga is the only known geothermal fluid with RAE sequence Cs > Li > Rb [3−6, 8−10]. The average increasing trend of major cations composition in Puga thermal waters follows as: Mg^{2+} (4 mg/l) < Li^+ (6.8 mg/l) < Ca^{2+} (11 mg/l) < K^+ (71 mg/l) < Na^+ (623 mg/l) and major anions composition follows as: F^- (12.9 mg/l) < SO_4^{2-} (131 mg/l) < Cl^- (424 mg/l) < HCO_3^- (855 mg/l). The average silica concentration is 144 mg/l. Thermal fluids have enrichment of B (~ 140 mg/l), F (~ 12.9 mg/l), Li (~ 6.8 mg/l), Cs (~ 8 mg/l) with molal ratio of Na/K < 10 which suggests Na^+ is depleted in thermal waters through action ion-exchange process or dilution with shallow groundwaters. The molal Na/Cl ratio is > 1 in all the thermal waters of Puga which suggests that high temperature fluids are repeatedly interacting with crystalline or volcanic rocks present in the ancient reservoir. The molal sum of ionic ratio, $(Ca^{2+} + Mg^{2+}) / (Na^+ + K^+)$, ranges between 0.03 to 0.06 which suggests active reverse ion exchange process and lower water flow course over carbonate rocks, or alkaline earths in hot fluids are exchanged with alkalis of aquifer rocks.

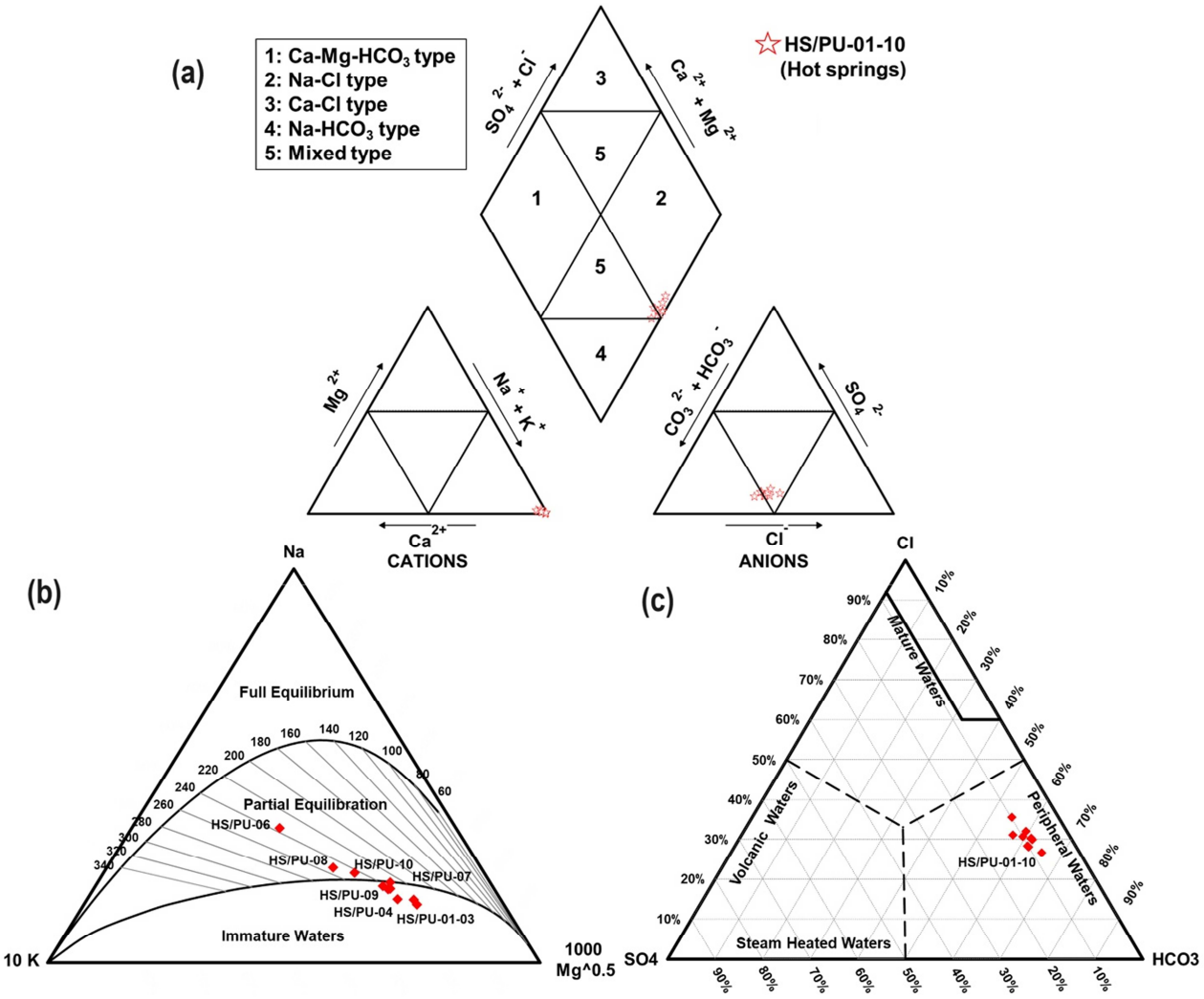

Figure 2. *(a) Piper trilinear diagram revealing genetic origin of thermal fluids; (b) and (c) Na-K-Mg and Cl-SO_4-HCO_3 diagrams unveiling the nature of geothermal waters of study area of Puga, respectively.*

4.2. Chemical Geothermometry

As the Na-K and K-Mg equilibration reactions are temperature dependent, cation geothermometers are formulated based on the ion-exchange reactions [22−25]. Geothermometers play a crucial role in assessing emerging fields and tracking the water dynamics of geothermal systems. As per Na-K-Mg diagram, most of the thermal waters fall in immature water domain, surviving various stages of partial equilibrium phase depending on extent of water-rock interaction (Figure 2b). As the hot fluids are discharged through geyseric manifestation with enrichment of Cl− ion, they retain deep seated reservoir information to a greater extent and such waters when used for reservoir temperature estimation, furnish temperature around 230−260°C, as per Na-K Giggenbach, Na-K Fournier and Na-K-Ca geothermometers. Inspite of geyser action, thermal waters are prone to mixing with local cold water, thereby making HCO3− ion as predominant ion composition and thus are peripheral in nature (Figure 2c). The reservoir temperature estimated from quartz geothermometry falls between 160−190°C which may be taken as the minimum temperature of reservoir as silica concentration in hot fluids is highly prone to dilution, boiling and precipitation. Taking fast equilibrating K-Mg geoindicators at shallow level and low temperature into consideration, reservoir temperature estimated in Puga is ~160°C which is in concordance with the reservoir temperature estimated from silica thermometry. This indicates that latest equilibration reactions have taken place in the reservoir at shallow level. Early studies by Shanker et al. have shown by considering reservoir temperature of ~255°C before steam loss and ~200°C of shallow reservoir that reservoir bears steam fraction of 0.2 with Cl content of minimum 375 mg/l before steam loss and 15% cold water blended with 85% of hot fluid component before thermal discharge on surface [11, 12]. The upsurge of fluids is preceded by conductive cooling at post-dilution.

4.3. Tracing Epithermal Mineralization

A large amount of silica gel with extremely tiny stibnite (Sb_2S_3) needles was ejected along with the discharge of hot fluids from many boreholes during the initial drilling phase at

Puga in Puga Multipurpose Project in 1970s [3−5, 9, 14, 17, 20]. In the breccia, there are similar stibnite needles. Amorphous silica gel containing nearly 2.2% Sb and traces of Ag, Au, Hg, Cu, and Pb made up the gelatinous material that was discharged from hydrothermal breccia during blow out. Later drilling phase by Oil and Natural Gas Corporation Limited (ONGC) Energy Centre in 2022 also encountered huge outburst of silica gel, along with fine stibnite needles from brecciated material [5]. Recent studies of hot spring deposits have revealed the occurrence of hydrothermal mineral, thenardite (Na_2SO_4), for the first-time in India, which serves as an indicator of paleo-climate and paleo-humidity [8]. Other significant hydrothermal minerals found in the study are jarosite, alunite, kaolinite, sassolite, and tincalconite. The surficial manifestations in the valley shows pockets of sulfur fumaroles, carbonate deposits and encrustations of borax along with several advanced argillic alteration zones signifying past acid magmatic activities. Evidence of polylithionite, which is Li-containing mica mineral, is observed for the first-time in thermal spring deposits of Puga and probably in India. According to Shanker et al., Cs-enrichment may have developed in Puga fluids during deep water circulation as a result of contact with Cs-rich rock, which is most likely a pegmatite with Cs present in biotite, beryl, or possibly even pollucite (a Cs-ore mineral) [11−14]. However, no any signature of Cs-containing mineral is evidenced in thermal spring deposits yet through powder X-ray diffraction studies. Thus, origin of Cs in thermal fluids may therefore be taken as magmatic. Other probable justification behind non-observation of any Cs-containing mineral in hydrothermal deposits could be high solubility of Cs-salts in hot fluids. Thus, occurrence of these epithermal minerals on surface of hot springs as deposits certainly confirms promising geothermal energy generation site in Puga.

4.4. Circulation Depth of Deep Fluid

The circulation depth of geothermal water of Puga is estimated using the following equation:

$$\text{Circulation Depth (H)} = \frac{Tz-To}{G} + Z_0,$$

where Z is the circulation depth (m), T_Z is the geothermal reservoir temperature obtained by geothermometer (°C), T_0 is the average annual temperature (°C), G is thermal gradient (°C/m), and Z_0 is the thickness of the constant temperature zone (m) [21]. In the study area, T_Z is obtained by silica geothermometer of 160°C, T_0 is around 10°C, G estimated from geophysical studies by Harinarayana et al. is 0.1°C/m and Z_0 is taken to be 0, estimated circulation depth is found to be 1.5 km. Hence, it can be claimed that as circulation depth of thermal water meets approximately 1.5 km depth, reservoir thickness should be greater than circulation depth [7, 18]. The results obtained from this technique is in consistency with the early studies by Harinarayana et al. where the magnetotelluric inversion studies brought out the presence of anomalous conductive zone at a depth of about 1.5–2 km [7, 18]. The geographic location of this conductive zone has boundaries between East and West and to extend more towards the North as compared to South of Puga valley. The area was exposed with past acid igneous processes, plutonic to submarine volcanic activities of Cretaceous age [8−10]. The anomalously high heat flow values (~536mW/m^2) prevailing in the area with highly localized conductive regimes, could probably be due to crustal melts from shallow to deep level which is acting as source of hydrothermal minerals and geothermal activity in the study area [10, 26].

5. Conclusions

In the present work, it has been illustrated how epithermal mineral signature can pave the pathway of determining potential geothermal energy resource assessment has been investigated. Studies highlight that thermal fluids of Puga are Na−Cl type with consistent abundance of conservative species, thereby, providing an explicit evidence of a single reservoir source of all the thermal discharges. The presence of polylithionite, a lithium-containing mica mineral, has been detected for the first-time in the thermal spring deposits of Puga, marking a probable first for India, which is the source of Li in thermal fluids. Circulation depth calculations show that meteoric water percolates at a depth of approximately 1.5 km depth, where deep fluid circulation and convectional solute assimilation take place before getting discharged as thermal waters. Anomalously high heat flow (~536mW/m^2) and observation of Cs-enrichment in thermal fluids certainly indicates none other than a cooling magma chamber at considerable depth as heat influx of thermal fluids and epithermal minerals.

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Conflicts of Interest

The authors declare no conflicts of interest.

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