SOURCE AND SIGNIFICANCE OF ANOMALOUSLY HIGH CESIUM IN GEOTHERMAL FLUID AT PUGA, LADAKH, INDIA

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SUMMARY - A comparison with some of the known geothermal systems of the world indicates that the Puga geothermal fluid has the highest relative concentration of Cs. The fact that the Puga fluid is the only known geothermal fluid with Cs>Li necessitates invoking processes in addition to normal water-rock interaction. It is possible that Cs, at least parhally, is of magmatic origin. Successful experiments have been conducted to extract Cs from geothermal fluid at Puga

1. INTRODUCTION

The Puga area, located at an altitude of 4400 m above m.s.l., in the Ladakh region of J&K state, hosts India's most promising and extensively explored geothermal field. About 5 km^2 of fault-bounded thermally anomalous area is covered by borax and other sublimates, and is characterised by the occurrence of more than 100 hot springs, varying in temperature from 30° to 84°C (local boiling point).

The Puga fluid is relatively dilute (TDS about 2400 mg kg^{-1}) HCO_3-Cl type water (HCO_3>Cl>>SO_4) with high F and B concentrations and molal Na/K of about 1 (Giggenbach *et* al., 1983). A unique and rather intriguing characteristic of the Puga fluid is that Cs exceeds Li and that total rare alkalies (RA) are anomalously high concentration (18 mg kg^{-1}). There is hardly any doubt that the bulk of its RA content has been acquired by the fluid at depths greater than 1 km through interaction with granitic rocks at temperatures exceeding 200°C. Preponderance of Cs in the Puga fluid, however, requires either the presence of a Cs-enriched rock in the reaction zone or an additional source of Cs supply.

2. RARE ALKALIES IN GEOTHERMAL SYSTEMS

It is rather interesting to note that in the earth's crust relative natural abundance of RA is Rb>Li>Cs, the average values being 90, 20 and 3 mg kg^{-1} (30:7:1), respectively (Taylor, 1966). In hydrothermal solutions, however, highly variable concentration levels of RA show a trend of Li>Rb>Cs. As the RA content of geothermal solutions would depend not only on the abundance of these elements in the rocks but also on their relative solubility, it may be inferred that the solubility of Li is markedly higher than that of Cs. Some of the earliest water-rock interaction experiments (Ellis and Mahon, 1977) showed that while Rb and Cs were liberated fiom rhyolite to solutions at temperatures and times sufficient to produce hydrothermal alteration, not much Li could be released from the rock. However, by keeping rhyolite particles in suspension in a rotating vessel at 300°C, solutions containing 22, 6.6 and 0.2 mg kg^{-1} of Li, Rb and Cs, respectively, could be generated. In a year long reaction between pumice breccia and Wairakie fluid at 215°C, the concentration of Li in solution increased fiom 10.5 to 20.5 mg kg^{-1}. In general, therefore, the experimental work has succeeded in generating solutions with RA at concentration levels similar to those in natural geothermal fluids.

Table-1 lists RA concentration in 25 geothermal areas of India, New Zealand and other countries (Ellis and Mahon, 1977; Ellis, 1979; Giggenbach et *al,* 1983; Henley and Ellis, 1983; Piovesana *et* al, 1987; Ravi Shanker, 1991), out of which 16 show the normal and more logical distribution pattern, *i.e.* Li>Rb>Cs. In 7 geothermal areas, including 4 from India (Pulga, Khirganga, Nathpa and Chhumathang), Yangbajing, Steamboat Springs and El Tatio, the observed trend is Li>Cs>Rb. *Cesano* brine has Rb>Li>Cs and Puga geothermal fluid has Cs>Li>Rb.

Ratios of Li and Cs to total RA concentration *are* plotted against one another in Figure 1. Puga stands out prominently as the only geothermal fluid with Cs>Li. Yangbajing fluid is closest to that of Puga in respect of Li/Cs ratio. Another feature that emerges is that the brines of Ahuachapan, Salton Sea, El Tatio, Cesano and Matsao plot in a field. Cesano fluid with Rb>Li>Cs, expectedly, has the lowest Li/Li+Rb+Cs value.

Table-1

Cesium and other Rare Alkalies (mg kg^{-1}) in some explored Geothermal Systems of the World

Sl. No.	Geothermal Systems	Source temp. °C	Li mg kg^{-1}	Rb mg kg^{-1}	Cs mg kg^{-1}	Total Dissolved Solids mg kg^{-1}
	India					
1.	Manikaran	130	1.2	0.15	0.15	600
2.		130	6.3	0.62	0.72	3200
3.	Khirganga	130	1.4	0.10	0.19	1170
4.	Vashist	120	1.2	0.16	0.16	850
5.	Tattapani	110	1.3	0.25	0.07	6400
6.	Jeori	110	2.4	0.37	0.14	2850.
7.	Nathpa	130	1.7	0.22	0.25	875
8.	Chhumathang	150	25.0	0.20	2.70	1250
9.	Puga	>200	7.5	1.15	9.30	2380
10.	Unhara	100	0.19	0.11	0.03	1900
	New Zealand					
11.	Nagwha	230	12.2	0.8	0.4	4450
12.	Broadlands	260	11.7	2.2	1.7	4000
13.	Wairakie	255	13.2	2.9	2.5	4600
14.	Rotokawa	220	8.2	1.1	1.1	3870
15.	waitapu	225	9.3	1.6	1.4	3600
	Other Countries					
16.	Yangbajing	220	9.4	1.1	5.0	1970
17.	Ahuachapan	225	8.0	6.0	2.7	18500
18.	Havergardi	215	0.3	0.04	0.01	1030
19.	Salton sea	340	215	135	14	263500
20.	Steamboat springs	160	5.7	1.2	1.9	2200
21.	Kizildere	200	4.5	0.0	0.33	4200
22.	El Tatio	255	47.5	8.6	17.9	16200
23.	Cesano	250	380	450	80	356000
24.	Matsao	245	26	12	9.6	22500
25.	Otake	220	4.5	1.8	0.7	2850

Dependence of RA concentration on lithological parameters is depicted in Figure-2, which plots ratios of Cs and total RA to TDS against one another. Low temperature Indian systems hosted by quartzites, carbonate rocks, gneiss and other crystallines have lowest ratios. New Zealand fluids, producing from more or less similar lithology comprising mainly rhyolite, ignimbrite and andesite plot in a cluster. Puga and Chhumathang in India and Yangbajing (Tibet, China), having reservoirs hosted by granitic rocks, are characterised by higher concentrations of total RA as well as of Cs alone.

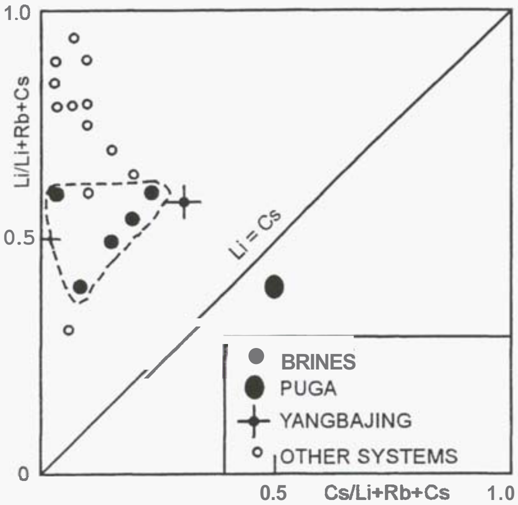

Figure 1- Plot of Li/Li+Rb+Cs versus Cs/Li+Rb+Cs Puga fluid is the only thermal discharge with Cs>Li Brines plot in a relatively small field.

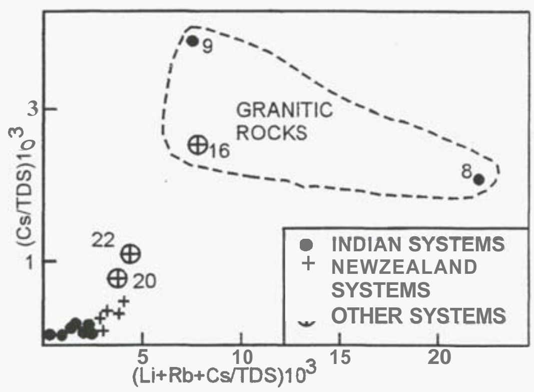

Figure 2- Plot of Cs/TDS versus Li+Rb+Cs/TDS. Systems hosted by granitic rocks have higher rare alkalies concentration. Puga geothermal fluid is characterised by the highest relative Cs concentration. For numbers, see Table-1.

3. SOURCE OF CESIUM IN PUGA FLUID

Out of 25 geothermal areas listed in Table 1, Cesano and Puga fluids are unique in having their RA contents dominated by Rb and Cs, respectively. While the former is one of the most concentrated hot brines known on the earth, the latter is a very dilute solution. High Rb in Cesano brine (Rb:Li:Cs = 5.6:4.7:1) is readily explained as potassic Monti Sabatini volcanic rocks in the region have 300 to 1200 mg kg^{-1} Rb contained mainly in a more reactive glassy matrix (Calamai *et al.*, 1976). By the same token, the Puga fluid (Cs:Li:Rb = 8.1:6.8:1) could have been generated as a result of interaction with a Cs-rich rock, which could most logically be a pegmatite with Cs contained in biotite, beryl or may be even in pollucite (Cs ore mineral). A simple calculation may be attempted to test this possibility. Taking a steady state discharge fiom Puga geothermal fluid at the rate of 30 ls^{-1} over a period of 10^6 years, about 10^7 tons of Cs is estimated to have discharged to the surface. Taking an anomalously high Cs content of 100 mg kg^{-1} in Puga granitoids, it may be calculated that Cs would have been completely leached out from about 40 km^3 of rock in the reaction zone. Considering the fact that rocks could not have been completely depleted in their Cs content and some of the aqueous Cs is likely to be taken up by hydrothermal minerals such as illite, the volume of the reacted rock would be even more. For a geothermal area of the size of Puga (about 5 km^2) even 40 km^3 of the reacted rock is unrealistically high. The simple water-rock interaction model for extraction of Cs fiom granitoids thus becomes rather preposterous.

Another possible way to explain the unique distribution pattern of RA in the Puga geothermal fluid is to infer the heat source in the form of a cooling acidic igneous body with a temperature of about 600°C at a relatively shallow depth of 5 km. The characteristic preference of RA to liquid phase and high volatility of Cs compared to that of Li and Rb would result in the observed distribution of RA (Cs>Li>Rb), when vapours emanating from the magmatic source would be absorbed by deep circulating geothermal fluid. Admittedly, no unequivocal evidence may be cited in favour of this magmatic model but in the absence of any other logical explanation for relative abundances of Cs and Li at Puga, it may be postulated that Cs and other RA may be, at least partially, of magmatic origin.

4. DISCUSSION

Only 4 geothermal areas, *i.e.* Salton Sea, Cesano, Matsao and El Tatio have Cs values more than that of Puga (Table 1). All these are moderately to highly concentrated brines with TDS ranging from 16,000 to 350,000 mg kg^{-1}. Taking the Cs/TDS ratio into consideration, the relative Cs of Salton Sea fluid is one of the lowest. At Cesano, Cs has probably been extracted from potassic volcanic rocks, which have also provided Rb to the system. At Matsao, Cs extracted from andesitic rocks has attained a level similar to that of Puga after concentration in the form of brine. At El Tatio, the source of RA probably lies in big biotite phenocrysts in the Puripicar Ignimbrite, the main producing level (see Lahsen and Trujillo, 1976). For its TDS, Puga geothermal fluid has the highest concentration of Cs in the world.

Similarities and dissimilarities in the behaviour of RA in the granite-hosted systems provide clues to the origin and retention of these cations in geothermal systems. While Puga and Yangbajing, with similar temperature, have a similar RA/TDS ratio, the former has Cs>Li. Chhumathang, a definitely lower temperature system (Table 1), has the highest relative concentration of RA and has a Cs/TDS ratio similar to that of Yangbajing. It is interesting to note that even at a temperature of 150°C, the Chhumathang fluid could extract about 28 mg kg^{-1} RA fiom granitoids, 90% of which is Li. Clearly, Li is the most soluble of the three RA and is released from the granite even in the absence of visible alteration. A very high concentration of Li in the Chhumathang fluid is probably related to the absence of illite and chlorite as alteration products of feldspars and ferromagnesian minerals, respectively, which are likely to consume substantially high quantities of Li. RA contents of the Chhumathang fluid may therefore be taken as close to that at the deepest reaction level.

At Yangbajing, higher Cs value is probably related to higher temperature. Li concentration, less than half of that at Chhumathang, is apparently due to fixation of Li in illite, chlorite and even hydrothermal quartz (see Goguel, 1983).

At Puga, a substantial quantity of Li might have been consumed by hydrothermal minerals as at Yangbajing. Although no wairakite, capable of consuming up to thousands of ppm of Cs (Goguel, 1983), is reported from Puga, some Cs might have been consumed by illite. Moreover, the fact that the top soil cover of Puga valley has $4x10^5$ kg of Cs deposited with borax as sublimate, indicates that the Cs concentration in the deep single phase fluid may be much higher than that analysed in the surface discharge. It becomes even more difficult then to account for Cs through water-rock interaction alone. This may be taken as indirect evidence in favour of some contribution of RA to the Puga fluid through magmatic sources.

5. POSSIBILITY OF EXTRACTION OF CESIUM

While 10 tons of Cs is being discharged annually by hot springs, about 400 tons of Cs is stored in the top 1 m of the soil cover of the Puga valley. Cesium has been concentrated from Puga thermal discharges by adsorption on ammonium 12-molybdophosphate (*AMP*) in the presence of Al^{+3} ions at pH of 6 to 7. Cesium-enriched extract has been obtained by dissolving Cs - *AMP* complex in the minimum quantity of 1 M NaOH. In another experiment, thermal waters were passed through Resorcinol Formaldehyde (RF) resin resulting in adsorption of Cs. Cesium was eluted from the resin by treating it with 0.75 N HNO_3.

6. CONCLUSIONS

Puga geothermal system is unique in the world in having the highest relative concentration of Cs, which is more abundant than Li. It appears that in addition to contributions due to water-rock interaction in granitoids at temperatures >200°C, some RA, particularly Cs, could have been added to the solution through magmatic source. Experimental studies have indicated that Cs may be extracted fiom thermal discharges.

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