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SHOCK BASALTIC GLASSES FROM LONAR LAKE, MAHARASHTRA: A POTENTIAL NATURAL ANALOGUE OF NUCLEAR WASTE GLASSES by B.K. Bajpai and P.K. Narayan. *Jour. Geol. Soc. India*, v.65(6), 2005, pp.775-777.

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I read this paper with special interest. I discovered that the authors did not mention some pioneering work in this area. I would like to bring some salient features of this work to their attention, so that the discussion would remain alive.

Ideally minerals used as nuclear waste hosts should be thermodynamically stable. A mineral which is thermodynamically unstable and has low laboratory rate, would well leach much faster in the field due to chemical or biological catalysts (Nesbitt et al 1981).

Under the financial assistance provided by AECL (Canada) and Swedish Government, we studied quaternary

rhyolite sample from Mono Craters, California. The rhyolite sample was found to be homogeneous in composition. We first studied the hydrothermal leaching and recrystallisation of rhyolite at temperature up to 300°C using not only the chemical leach monitors of weight loss and solution analysis, but also modern surface probes such as SEM (Scanning Electron Microscopy), ESCA (Electron Spectroscopy for Chemical Analysis) and SIMS (Secondary Ion Mass Spectroscopy). We observed that *congruent dissolution* was the major mechanism of leaching (Karkhanis et al 1979, 1980).

Then we studied the electrical conductivity and leaching behavior of natural rhyolite glass and synthetic aluminosilicate glasses prepared by addition of fluxing agents such as Na₂O and CaO to the natural rhyolite composition (Allanatt et al 1983). Frequency-dependant a.c. conductivity measurements showed that the conductivity is governed essentially by Na⁺ mobility and that this depended on Ca²⁺ concentration. At the intermediate

temperature (100° and 200°C) *congruent leaching* becomes more important, while incongruent dissolution and indeed quasi-equilibrium state is important at 25° C

For a nuclear waste disposal system one has to consider the whole geochemical system (*Waste form-buffer-host rock*) We therefore studied sodium-calcium aluminophosphosilicate glasses and its hydrothermal leaching behavior (Karkhanis et al 1980, Melling et al 1983) This tailored glass gave particular minerals as its leaching products under specific condition They were capable of retaining some fission products (Cs and Sr) in their structure

It is important to understand here that none of these solutions, including the shock glasses from Lonar Lake can be touted as magic bullet that will be the panacea for all the situation that we may encounter while managing the nuclear waste

(Ringwood et al 1979a, 1979b) introduced SYNROC process Three minerals were used as hosts — *Perovskite* (CaTiO_3), *Ba-Hollandite* ($\text{BaAl}_2\text{Tl}_6\text{O}_{16}$) and *Zirconolite* ($\text{CaZrTi}_2\text{O}_7$) It was reported that these minerals are kinetically stable in extreme hydrothermal conditions (900°C and 5000bar) It was therefore suggested as a host for nuclear waste

We did some fundamental thermodynamic and kinetic work in order to look at the stability of perovskite both in rock matrices and natural waters (Nesbitt et al 1980, 1981a,b) Our results showed that perovskite is kinetically unstable in the presence of common silicates Geological evidence from common alkaline rocks also indicates that hollandite and zirconolite probably will not survive common rock matrices

R.K. Bajpai and P.K. Narayan, Bhabha Atomic Research Centre, Trombay, Mumbai – 400 085, *Email: rkumar@apsara barc ernet in*, reply

We thank Dr Karkhanis for his interest in our paper The contributions of Mr Karkhanis towards chemical durability of rhyolitic glasses is well known But it is now well established that basaltic glasses are more akin to nuclear waste glasses being currently used for immobilization of

nuclear wastes worldwide Hence we restricted our discussion to only basaltic glasses as they have compositions closer to waste glasses being used in India In greater part of his comments, he has given summary of his work on rhyolitic glasses and has not raised any specific query regarding our note

As regards to his observation that such glasses cannot be touted as magic bullet that will be the panacea for all the situations that we may encounter during radioactive waste management, we wish to make it very clear, that though glasses are known to be thermodynamically unstable phases, they are still being preferred as matrix of choice world over today In India also, there are two operating plants where waste is being immobilized in such glasses on commercial scale Another third one is likely to commence production shortly This is mainly because of very homogeneous compositions, good waste loading, very low permeability, ease of commercial production and low production cost As radioactive wastes will remain hazardous over thousands of years even after their disposal in a deep geological repository, vitrified wastes are hosted in SS canisters to provide additional safety These canisters are further placed in another SS overpack In deep geological repository, layers of clays and sand and clay admixtures will surround these overpacks These multiple layers together known as engineered barrier will ensure confinement for thousands of years The shortcomings of a glass matrix is thus taken care by providing this additional protection After their failure, host rock will isolate waste from environment for extended geological periods

At BARC, leaching tests have been carried out on such glasses under controlled conditions for short duration Extrapolation of these results to thousands of years is possible to some extent by numerical geochemical modeling The only possible way to validate such models is through natural analogues In the paper, we only projected the possibility of using shock glasses as natural analogues for validation of experimental results on alteration rates, mechanism, and alteration products The work on SYNROCK is mostly under R&D phase even today in most of the countries and commercial production is yet to commence

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NEW OCCURRENCE OF MANGANOCOLUMBITE FROM LATE PROTEROZOIC PEGMATITES OF BHURPIDUNGRI, JHARSUGUDA DISTRICT, ORISSA by P. Jagadeesan, K.S. Mishra, and P.V. Ramesh Babu. *Jour.Geol. Soc. India*, v.66, 2005, pp.141-144.

S. Viswanathan, Flat B-203, Block-B, United Avenue Apartments, South End, 7-1-29, Ameerpet, Hyderabad-500 016, comments:

The authors claim that they are reporting for the first time, the occurrence of manganocolumbite in the pegmatites of India at Bhurpidungri in the Jharsuguda district of Orissa. This claim cannot be accepted for the following reasons: Two criteria have to be fulfilled for naming a member of the columbite-tantalite isomorphous series as ‘manganocolumbite’: (1) an MnO/FeO ratio of more than 3 and (2) a Ta₂O₅ content of less than 20 percent by weight (Vlasov, 1966, p.453; Kuz'menko, 1959, in Vlasov, *op.cit*). Kuz'menko and Vlasov also feel that the term ‘manganocolumbite’ should be reserved only for the manganese end-member of the columbite-tantalite series, MnNb₂O₆.

In Table 2 on p.143, the authors have given analytical data for eight samples of columbite-tantalite, numbered BP/1 to BP/8, from Bhurpidungri. As they have not given the MnO/FeO ratio of the samples, and also overlooked the significance of these ratios, I have calculated the MnO/FeO ratios. Seven of the samples (BP/1, 2, 4 to 8) have MnO/FeO ratios of less than 3, with BP/5 having a very low value of 0.86. Although one sample (BP/3) has an MnO/FeO ratio of

3, its Ta₂O₅ content is high (24.45%). The average of the eight samples (BP_x) has an MnO/FeO ratio of only 2, though its Ta₂O₅ content is 14.33%. Therefore, the Bhurpidungri columbite-tantalites are not ‘manganocolumbites’.

On p.144, the authors state that, “The manganocolumbite under study contains up to 18.46% MnO, and is comparable with that from the San Diego Mine, Mesa Grande, California (MnO - 19.21%) and Pakeagama pegmatite, Ontario, Canada (MnO - 12.50%) (Breaks et al. 1998) (Table 3).” This comparison is misleading because, when comparing ‘manganocolumbites’ from different areas, it is not enough to compare only their MnO values. It is absolutely essential to compare their MnO/FeO ratios and Ta₂O₅ contents. For instance, with its very high MnO/FeO ratio of 55.06 and Ta₂O₅ of 12.56%, the San Diego Mine sample is a fine example of a manganocolumbite. In sharp contrast, with its low MnO/FeO ratio of 2.17 and high Ta₂O₅ of 30.99%, the Pakeagama sample is not a manganocolumbite. As already pointed out, the ‘average’ Bhurpidungri sample is also not a manganocolumbite because of its low MnO/FeO ratio of 2.

If the MnO content of a columbite-tantalite is the only criterion for naming it as ‘manganocolumbite’, as the authors appear to believe, they should note the following: