## Komatiites through time reflect trends in mantle incorporation of meteoritic platinum group elements

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The temporal changes in the concentration of platinum group elements (PGE) in a rare type of volcanic rocks called komatiites have provided new information on earth's core formation and mantle differentiation. These rocks are derived from high temperature melts of ultrabasic composition, mostly formed early in earth's history, when accreting meteorites had not ceased bombarding the earth. They occur most abundantly in greenstone belts of the Archaean eon (3.6-2.5 G yr old) and somewhat less in the Proterozoic (2.5-0.54 G yr old) and rarely in the Phanerozoic (<0.54 G yr old) eons. Komatiites were first discovered in the late 1960s from the 3.49 G yr old Komati Formation, Onverwacht Group in Barberton Mountainland, South Africa<sup>1</sup>. Following this South African discovery, new finds of komatiites were reported from the Archaean and Palaeoproterozoic greenschist belts in Australia, Canada, Zimbabwe, Brazil, Russia, Finland, Baltic Shield, North China and from the Phanerozoic (Permian-Triassic) Song Da zone of NW Vietnam, from the Cretaceous age Gorgona Island (off the Columbia coast), and Costa Rica. In India, komatiites were first reported from the Archaean Iron Ore Group of Singhbhum Belt<sup>2</sup> and subsequently more occurrences came to light from the Archaean-Proterozoic Dharwar Craton, Kolar Schist Belt, Nuggihalli Greenstone Belt, Bhundelkhand Craton and from the younger Mesozoic period Permian Ladakh region.

Most of the komatiites have a characteristic spinifex texture consisting of bladed olivine or pyroxene crystals set in a glassy groundmass. Many of these rocks are altered by low-grade metamorphism, their glassy groundmass devitrified, the olivines replaced by tale and serpentine, the pyroxenes to chlorite, tremolite or epidote. Komatiites exhibit unusual chemistry - high MgO, very high MgO/FeO ratio, low alkalis, TiO2 and Al<sub>2</sub>O<sub>3</sub>/CaO ratio; this composition also varies depending on the depth of formation, mantle condition and progress of geological time3. Komatiites are also broadly divided into (i) Al-depleted type having low  $Al_2O_3$ , low  $Al_2O_3/TiO_2$  ratio of <12,  $CaO/Al_2O_3$  ratio of  $\sim2-2.5$ , present mostly in  $\sim3.5-3.0$  G yr old Barberton Belt and Pilbara Craton and rare in belts less than 3.0 G yr (ii) Al-undepleted types characterized by  $Al_2O_3/TiO_2$  ratio of  $\sim20$  and  $Cao/Al_2O_3$  ratio of  $\sim1$ , and abundantly occurring in  $\sim2.7$  G yr old greenstone belts of Canada, Zimbabwe and Australia but rare in belts of older ages<sup>4</sup>. Most of the 3.35 G yr old Komatiites from the Dharwar Craton, India are Al-depleted and only few are Al-undepleted<sup>5</sup>.

According to conventional thinking, Archaean to early-Proterozoic komatiites are produced in deep mantle dry plume environment near the core-mantle boundary (hot spot magmatism), where the melting temperature is estimated to exceed 1800°C (refs 6 and 7). Komatiites are also known to form at shallow mantle depths in a subduction environment, where the presence of water effectively lowers the melting temperature 7,8 (~1600-1500°C). Their origin in different mantle environments, such as deep mantle 'dry' conditions and shallow mantle 'wet' conditions have prompted considerable debate as they have implications for the interpretation of Archaean earth and its thermal evolution<sup>8</sup>.

A geochemical trend, missed until now, exhibited by platinum group elements (PGE) - Os, Ir, Ru, Pt, Pd, Rh, Re, in the komatiites formed at different periods of earth history, investigated in a recent study<sup>9</sup>, has shed fresh light on mantle dynamics. During partial melting of the mantle, Os, Ir and Ru behave compatibly and partition into the solid phase, whereas Pt, Pd, Rh and Re which are incompatible prefer the melt portion. Selecting one element, Pt to represent the rest of the incompatible PGE group and likewise Ru to represent the compatible group, their temporal concentrations in the Komatiites were examined. Published PGE concentration data from global Komatiites from belts and cratons belonging to the Archaean to Mesozoic period and free from Ni-sulphide mineralization that could have incorporated some PGE from the melt were studied.

Among these, except for a few 3.5-3.2 G yr old samples from Barberton and Pilbara, most of the samples were from the late Archaean (~2.7-2.9 Gyr) or early Proterozoic spans (2.0-2.5 G yr). In samples having about the same amount of MgO, though PGE in the early Archaean samples were notably depleted, they showed enrichment progressively in younger ages. While Pt and Ru were a low ~2-5 ppb in Barberton and Pilbara samples, moderate amounts of ~8 ppb Pt were seen in those from Canada, Zimbabwe, South Australia and Russia and high ~8-10 ppb in the Mesozoic komatiites from Gorgona Island and Quebec (Canada). The most severe depletion was noticed in the oldest (>3.5 G yr) samples from Barberton and Pilbara. Interestingly, within the same Archaean occurrence, the sequentially older ones among them showed more PGE depletion than the relatively younger ones, irrespective of whether they were Al-depleted or Al-undepleted, thus highlighting existence of a good correlation between age and PGE contents9.

Before arriving at the most plausible mechanism for the diminishing PGE, progressively back in geological time, the latest study considered the viability of several mantle processes that could have led to this trend<sup>9</sup>. For example: (i) the ascending early Archaean komatiite plume melt may have achieved sulphide saturation by crustal contamination resulting in PGE depletion; but the study rejects this possibility as the samples were chosen from occurrences having no links to sulphide mineralization. Further, the high pressure of the deep lower mantle under which early Archaean Komatiites were formed will inhibit sulphide solubility in basic-ultrabasic magmas.

(ii) The possibility of influx of low PGE bearing eclogite component into the early Archaean mantle is another mechanism considered. But, this plate tectonic introduction is also improbable as this would require as much as 60% addition of this component, which is highly inconsistent considering the high MgO (>18%) content of these komatiites. Further, contrary to expectation, PGE deple-

tion is absent in certain 2.9 G yr old komatiites, known to be derived from eclogite enriched source, in comparison to other 2.9–2.7 G yr old komatiites.

- (iii) Development in subduction-related wet mantle zone is yet another process that has the potential to bring about the early Archaean PGE depletion. However, such an origin for these rocks is also doubtful considering the absence of trace element signatures characteristic of such environments in early rocks of this age.
- (iv) Similarly, the PGE enrichment in younger age samples may be a consequence of evolution in an incompatible-element-depleted mantle source arising either due to extraction by developing continental crust or due to partial melting followed by gravitational separation of eclogite component. Neither the theoretical calculations of the partial melting pressures that could have operated nor the proposed extraction by the continental crust favour development of this trend observed in the komatiites through time.
- (v) The possible derivation of the early Archaean komatiites from a stratified layer enriched in PGE-poor majorite (garnet) formed in the early magma ocean, 4.5 G yr ago, is also deemed not tenable. Such komatiites should then be confined to Al-depleted >3.2 G yr old early Archaean samples only, but this feature is seen also in Al-undepleted varieties of the same age.
- (vi) Another likely mantle mechanism leading to depletion in early age komatiites is the possible formation in the

relatively low oxidation state of this period because such a mantle would retain S as sulphides and PGE mostly alloyed in the source itself relative to more oxidized late Archaean and Proterozoic mantle. However, the contemplated increase in the oxidation state in such a short-time interval between Archaean and Proterozoic is unlikely since the mass of oxygen available in the crust and atmosphere was hardly sufficient to boost the oxidation state of the mantle of those times. Neither is the latter state supported by V and Cr, two of the redox sensitive metals whose concentrations are about the same level in the basalts of both Archaean and modern times.

The latest study now attributes that core formation, 4.55 G yr ago, is responsible for the depleted PGE in the early Archaean komatiites. During this process, all PGE from the early-accreted meteorites were drawn into the core alloyed with Ni-Fe, thus depleting the early-formed mantle. Consequently, these early age komatiites that initiated at the core-mantle boundary register the depleted PGE state of the deep mantle with a low Pt and Ru, almost close to 0. After core separation, there was continued influx of PGE to the earth through late accreting meteorites - the wellknown 'late veneer', till about 3.8 G yr ago. These PGE additions from the late veneer progressively enriched the upper mantle and were transported slowly to the lower mantle in the succeeding 1.5 G yr and this is reflected in the komatiites formed around 3–3.2 G yr ago. By 2.9 G yr ago, the study argues, the lower mantle had equilibrated with the late veneer producing PGE concentration close to modern primitive upper mantle. With the progress of geological time and mixing-up of the meteorite-sourced PGE, their concentration gradually homogenized in the entire mantle.

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