IRIDIUM IN MARINE SEDIMENTS: ANALYSIS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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The geochemistry of iridium has stimulated interest in recent years due largely to questions concerning its enrichment in sediments at the Cretaceous-Tertiary (K-T) transition. Iridium is 10^3 - 10^4 times more concentrated in chondritic meteorites than in average crust and has therefore been used as a proxy for the flux of cosmic material to the earth. Since the initial discovery of the K-T Ir spike at Gubbio, Italy, Ir enrichments have been found at several other sites which record this event, and at other biostratigraphic boundaries as well. The apparent relationship between meteorite impacts and intervals of mass extinction has fueled debate about the nature of extinction events. Despite the importance of Ir in examining this question, little is known about its geochemistry. This project has been undertaken to elucidate the behavior of Ir in marine sediments during early diagenesis.

During the last several months a technique has been developed to measure Ir in sediments by isotope dilution ICP-MS. The sediment is initially spiked and dissolved using all-teflon bombs in a modified microwave oven. Ir is preconcentrated on an anion exchange resin (Biorad, AG1x8), eluted with hot nitric acid and analyzed on a VG Plasmaquad ICP-MS. The final 0.25 mL sample is introduced into the plasma using flow injection and a conventional nebulization system. The major isobaric interferences for Ir are $^{177}Hf^{16}O$ and $^{175}Lu^{16}O$. The anion exchange step reduces the concentrations of Hf and Lu in the sample by a factor of 100 or 1000, respectively, which reduces the interference of their oxides to about one percent of the Ir signal.

Initial results for two Black Sea cores which were taken at the same site, 20 years apart, show that Ir concentrations in the Recent sapropel (Unit II) are somewhat variable and are correlated with Mn concentrations in the older core. Because of poor preservation of the older core, interpretation of this correlation is not possible without further data. An intensive study is underway to determine the relationship among Ir and other transition metals in additional Black Sea cores.

HF ISOTOPE SIGNATURES OF ZIRCONS BY ION MICROPROBE

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Within-grain U-Pb age determination of zircon using the ion microprobe SHRIMP has revealed a new petrogenetic world of inherited zircon xenocrysts and metamorphic zircon overgrowths. Our aim now is ion probe determination of zircon Hf isotopic compositions to specify the geochemical nature of magma sources and parental fluids. We have made useful progess but formidable instrumental problems remain. The first arises from the high ionization potential of Hf, which results in a yield of $^{176}Hf^{16}O^+$ of only *ca.* 3 x 10^4 cps at 3000R. Only precise $^{176}Hf/^{177}Hf$ measurements, $\leq$.05%, are useful geochemically, demanding that at least 3 x 10^7 $^{176}Hf^{16}O$ ions must be counted, which requires long measurement periods. At least four mass channels must be recorded in addition to 192 and 193: 191 is required to strip ^{176}Lu and 190 to strip ^{176}Yb, 196 to use $^{177}Hf/^{180}Hf$ for mass- fractionation correction, and either 197 or 189 to correct for hydroxides. A second problem is the dynamic range of the counting system: the most abundant $^{180}Hf^{16}O^+$ can exceed its linear range, which compounds errors in the peak-stripping process.

For a single 2 hour run, the precision obtained so far for the corrected $^{176}Hf/^{177}Hf$ is typically 0.1% (σ). By replicate measurements at this precision, we have determined that Hf in the 4.2 Ga Mt. Narryer zircons and other younger Archaean zircons formed in sources having chondritic Lu/Hf, whereas a number of post-Archaean zircons originated in Lu/Hf enriched sources. On the other hand, a 570 Ma old Sri Lankan zircon was depleted in ^{176}Hf by 0.23%, implying an origin from metamorphosed Archaean crust.

SUBSTITUTION OF GOLD INTO THE CRYSTAL STRUCTURES OF ARSENOPYRITE AND PYRITE.

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Arsenopyrite and pyrite have been identified as the most important sulfide hosts for solid solution gold in a number of refractory gold-bearing ores. Gold concentrations in arsenopyrite range up to several thousand parts per million. Gold concentrations in pyrite are generally lower but may exceed 100 ppm.

A positive correlation between the gold and arsenic concentrations in pyrite is interpreted as suggesting that the presence of As can facilitate the substitution of Au into a sulfide mineral.

A clear answer as to whether Au may substitute our indirect evidence supports the view that Au replaces the excess As which occupies Fe sites and that gold-bearing arsenopyrites are commonly also As-rich. A similar mechanism may also operate for pyrite, where a threshold concentration of As (about 0.2-0.4%) needs to be present before significant Au may be incorporated into the structure.

SECONDARY DISPERSION AND FIXATION OF Pd, Pt AND Au SURROUNDING A Pd-Pt PROSPECT IN QUEBEC

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Rocks, soils and lake sediments, as well as lake and groundwaters around the Pd-Pt enriched Cu-Ni prospect at Lac Sheen, Quebec have been determined for their concentrations in Pd, Pt and Au.

The media samples are anomalously enriched in these elements relative to those from other areas in the vicinity believed to be unmineralised. These results show that Pd and Pt are mobile in the secondary environment and may offer a geochemical means of exploration for other PGE-enriched deposits.

The markedly different solution chemistry of Pd and Pt in the supergene environment is illustrated by the preferential enrichment of Pt in soils and lake sediments (X-XO ppb) compared to Pd (0.X-X ppb), whereas the reverse appears true for the lakewaters, where concentrations of Pd (XOO parts per trillion) are an order of magnitude greater than for Pt (XO ppt). The behaviour of Au tends to follow Pt with fixation in soils and sediments.

THE HISTORY OF ANOXIA AND EUTROPHICATION IN CHESAPEAKE BAY AS DOCUMENTED IN THE STRATIGRAPHIC RECORD

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Stratigraphic records preserved in the sediment are being used to reconstruct the history of sedimentation and water quality of the Chesapeake Bay, including anoxia and eutrophication. Four cores of bottom sediments were collected along a transect across the Bay near the mouth of the Choptank River, in areas that are always anoxic as well as areas that are sometimes anoxic. Bottom sediments of the cores yeild C^{14} dates of 910 to 2650 years before present. Pollen, diatoms, and total organic carbon (TOC) are used as indicators of environmental conditions. Diatoms, unicellular algae with a silica shell readily preserved in estuarine sediments, are useful palaeoecological indicators of light availability, temperature, salinity, nutrient and oxygen availability, and pollutants.

Data collected show that diatom centric/pennate ratios increase since European settlement from below one to as much as four. Some benthic species disappear from the sedimentary record since around 1930, and planktonic species increase steadily. Sediments dated prior to 1650 (pre-European) show sedimentation rates as low as 0.03 cm/yr and TOC fluxes of 1.3%/gm/yr. Since that time, sedimentation rates average 0.21 cm/yr and TOC fluxes are up to 3.9%/gm/yr. Two peaks in TOC are noted, one between 1800 and 1860, and one from around 1940 to the present time.

Analysis of the data indicates that sedimentation rates, anoxic conditions, and eutrophication have increased dramatically in the Chesapeake Bay since the time of European settlement.

$^{40}Ar/^{39}Ar$ DETERMINATIONS OF COOLING, DENUDATION, AND UPLIFT RATES IN THE GANGDESE BATHOLITH, SOUTHERN TIBET

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Since the beginning of the Indo-Asian collision at ~40 to 50 Ma, the Cretaceous to Eocene Gangdese batholith in southern Tibet has experienced total unroofing of between 11 and 7 km. The 42 Ma Quxu composite pluton, near Lhasa, yields a cooling history highlighted by a brief interval (~2 Ma) of very rapid unroofing (>3 mm/a) beginning at 20$\pm$1 Ma. Additional sites from this pluton have been studied: two sites yield cooling histories which are essentially identical to the earlier results, but a third location, close to the southern margin of the batholith, has a $^{40}Ar/^{39}Ar$ biotite age of 42 Ma and a K-feldspar age spectrum with a gradient from 29 to 42 Ma; the history of this latter sample is largely due to cooling of the pluton against cold country rocks. Available data suggest that different parts of this composite pluton were intruded over an interval of 8 Ma at different levels in the crust; the cooling and uplift histories of the various parts of the pluton suggest N-S hinged unroofing within the belt of granitoid rocks. The current level of exposure dipped northward 10° between 37 and 25 Ma. 80 km to the W of Quxu, the Pachu granite yields concordant biotite and K-feldspar ages of 14-13 Ma from three samples. The K-feldspar age spectra from all three of these locations are flat and reflect cooling from ~335 to ~200°C in less than 1.5 Ma. It is most likely that this brief interval of rapid cooling is also related to rapid denudation (>3 mm/a) - perhaps the same episode recorded in the Quxu or a separate, younger event. K-feldspars from Late Cretaceous(?) volcanic rocks yield slow cooling gradients between 55 and 40 Ma indicating burial to depths >7 km and subsequent cooling rates of only ~6°C/Ma prior to and during the initial phase of collision. This suggests to us that the Gangdese Belt was not to any significant extent isostatically adjusting to denudation or thickening prior to the Early Miocene. Because drainage is antecedent to topography, much of the rapid denudation we observe must have been associated with uplift relative to the geoid. The cooling of rocks from mid-crustal levels will produce mineral ages which lag behind the onset of uplift, but only by about 1-2 Ma for rocks exhumed from depths of 7 to 11 km.

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