water to magmatic gas of less than 1.1 are required to raise the lake level on the order of 1-10s meters. Such water levels may allow water to drain down the outer crater walls. The water level begins to drop once the expanding fluid looses sufficient heat to the lake water. Lake water that was pushed up along the inner crater walls begins to drain back down and into the conduit. The downward motion of the lake water and upward movement of steam collide to generate a pressure wave in the atmosphere. This sequence of events though generated from a simple eruption scenario, may be one of the mechanisms for lahar generation (Mt. Ruapehu volcano, N.Z.), updoming of the sea or lake surface prior to eruptions (Ritter Island, Papua N.G., Mt. Ruapehu volcano, N.Z.), and rapid evaporation of crater lakes observed during crater lake eruptions (Mt. Spurr, Alaska). The sequence of event becomes more complex when the walls deform, magma rises through the crater and a thermal source is used to pressurize the conduit prior to eruption. All results will be presented in a series of parametric animations.

V51C MCC: Level 1 Friday 0830h

U-Series in Continental Environments: Soils, Rivers, and Groundwaters II Posters *(joint with H)*

Presiding: **B Bourdon,** Institut de Physique du Globe de Paris**; F Chabaux,** Université de Strasbourg**; D Porcelli,** University of Oxford

V51C-0303 0830h POSTER

Interest of 238U-234U-226Ra Disequilibrium for Tracing Groundwater Inputs Into Surface Waters: A Case Study

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Characterization of deep water inputs into surface waters requires geochemical tracers that develop different signatures in surface and ground waters. It has been suggested that U activity ratios could play such a role (e.g. Riotte et Chabaux 1999). Here we propose to test this hypothesis in the case of the Lauter stream (East France-West Germany), a stream that drains sandstone of the Bundsandstein sequence, in which several superimposed and more or less independent aquifers are developed. Major elements, trace elements, Sr isotope ratio and 238U-234U-226Ra disequilibrium have been analysed in the dissolved load of water samples collected in the Lauter stream and in the different groundwaters of the sandstone formations. The data certainly give the first convincing demonstration of the usefulness of U activity ratios in surface waters to quantify the influence of deep waters upon surface waters. The data point out that, in the specific case of the Lauter stream, more than 50% of the total dissolved load carried by the stream is supplied by deep waters. This contribution significantly modifies the 226Ra/238U activity ratio, which in turn suggests that 238U-226Ra disequilibria could also be helpful for discriminating in the global chemical fluxes carried by rivers, those representative of surface weathering processes. Overall these results highlight (1) the necessity to distinguish surface weathering fluxes from deeper ones in order to establish realistic weathering budgets at the scale of a watershed from chemical analyses of river waters and (2) the potential of 238U-234U-226Ra disequilibria to perform such distinction. Riotte et Chabaux (1999) Geochim. Cosmochim. Acta 63 1263-1275

V51C-0304 0830h POSTER

^{238}U-Series in Fe Oxy/Hydroxides by LA-MC-ICP-MS, New Insights Into Weathering Geochronology

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The establishment of a geochronological framework for weathering processes is essential for an understanding of the evolution of the regolith and its dynamics. However, there are few robust answers regarding the absolute age of weathering and its rates. Nowadays, ^{40}Ar/^{39}Ar analysis of Mn-Oxides (cryptomelane) and K-bearing secondary sulphates have provided one of the few generally reliable chronometers (e.g. 1), but is restricted to high-K secondary phases. This work presents a different approach to obtain geochronological information from weathering minerals, namely measurement of ^{238}U-series disequilibria in authigenic Fe oxy/hydroxides. These may be potentially useful recorders of weathering processes as they commonly occur as weathering products and have high affinity towards dissolved uranyl complexes. Furthermore, U-Th fractionation during weathering has been extensively reported [2], effectively resetting the U/^{230}Th geochronometer. LA-MC-ICP-MS facilitates in situ measurement of ^{238}U-series disequilibria in authigenic microcrystalline iron oxy/hydroxides (precipitated between cracks and veins in partially and heavily weathered chlorite-muscovite schist) and pisoliths (ferruginous concretions). Contrary to previous studies [e.g. 3], in situ measurement of ^{238}U-nuclides enables selective analysis or iron oxy/hydroxides phases, minimizes contributions from allogenic phases and, reduces the need of mathematical corrections to obtain the activity ratios for the authigenic phase [4, 5]. The results suggest that supergene iron oxy/hydroxides are good recorders of weathering processes; they precipitate during the early stages of weathering, reflect the U-isotopic composition of the groundwater, appear to act as closed-systems in weathering conservative environments, and behave in a predictable fashion when subjected to intense weathering and leaching conditions. The ^{230}Th-ages of the iron oxy/hydroxides indicate that the timing and intensity of weathering appears to be largely controlled by global climatic changes, suggesting that weathering rates have not been constant during the last 300 ka in Northern Australia. References: 1 P.M. Vasconcelos. Annual Review in Earth and Planetary Sciences 27(1), 183-229, (1999) 2 M. Ivanovich and R.S. Harmon, Uranium-series disequilibrium : applications to earth, marine, and environmental science, xxxiv, 910 pp., Oxford University Press, Oxford, (1992) 3 S.A. Short, R.T. Lowson, J. Ellis and D.M. Price. Geochimica et Cosmochimica Acta 53, 1379-1389, (1989) 4 K.R. Ludwig and D.M. Titterington. Geochimica et Cosmochimica Acta 58(22), 5031-5042, (1994) 5 Luo, S. and T. L. Ku. Geochimica et Cosmochimica Acta 55(2): 555-564. (1991)

V51C-0305 0830h POSTER

Origin of the dissolved U-Sr fluxes in the Himalayan rivers: cases of the Indus, Ganges and Brahmaputra

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The rivers draining the Himalaya are recognised as major contributors to the dissolved riverine flux to the oceans, with a non-negligible effect on the global budget of elements such as Sr and U. The precise characterisation of the different sources contributing to these fluxes is important and has to be done to model correctly the Himalayan river chemical flux variations through time, in response to climatic or tectonic variations and to better constrain the impact of these rivers on the U and Sr oceanic budget. The recent study of the Ganges watershed has shown the potential of the U-Sr combined isotopic analyses to reach this objective (Chabaux et al., 2001). We propose to extend this approach for the two other main Himalayan rivers: the Brahmaputra and the Indus. Our results show that the U and Sr fluxes carried by the Brahmaputra are not only controlled by the Himalayan end-member identified during the study of the Ganges watershed, but also by a chemical flux coming from the Tibetan plateau and another one specific of the plain formations. These two latter fluxes contribute to the U and Sr dissolved budget of the Brahmaputra during the dry season, and at different intensities for these two elements. During the monsoon, their impact seems to be negligible compared to the flux coming from the Himalayan chain. As a first approximation therefore, the annual hydrological cycle of the Brahmaputra river would have a U-Sr systematics very close to that of the Ganges river. By contrast, for the Indus River, in addition to the Himalyan flux, U and Sr dissolved budget is significantly affected by chemical fluxes from the Tibetan plateau, the plain and also from the West Pakistan Fold belt. The input of the Punjab river, the main Indus tributary that strongly influences the U-Sr budgets, on the Indus can be explained in terms of mixing between the Himalayan and the plain end members. These results will be used to constrain the response of U and Sr fluxes of the Himalayan river system to climatic variations and to discuss the impact of these variations on U and Sr oceanic budgets. Chabaux F., Riotte J., Clauer N. and France-Lanord C. (2001) GCA 65(19), 3201-3217

V51C-0306 0830h POSTER

Controls on d234U in surface waters of the South Island of New Zealand

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The development of new proxies with which to assess the interconnection of climate and continental weathering is important because of the role of silicate weathering in the long-term carbon cycle. A potential proxy of both modern and past weathering regimes is the U isotope ratio 234U/238U (expressed as d234U). River water is nearly always enriched in 234U, due to release of alpha-recoil mobilised 234U from continental rocks. High d234U values may be expected in areas where this recoil 234U can build up, or where fresh mineral surfaces are continually being exposed. The South Island of New Zealand is an ideal place to investigate the dominant controls on riverine d234U since it has a wide range of uplift rates and climate environments. We have analysed U concentration and d234U in more than 30 surface-water samples by MC-ICP-MS. These samples include rivers, lakes, groundwater and glacial melt. The concentration of U in both glacial ice and ground waters is low, so the dominant source of U in surface waters is from weathering. The d234U values are extremely variable (68 to > 3600) and display some of the highest values that have been observed. The bedrock chemistry is reasonably uniform so this range in d234U is not a function of changing lithology. The d234U values are, therefore, controlled only by the production rate of mobile 234U and its susceptibility to removal by river water. A clear positive relationship between river d234U and uplift rates is observed, suggesting that physical weathering is an important control on d234U. For instance, the samples with the highest d234U values (2800-3600) are from the zone of maximum uplift on the dry east coast, whereas low d234U values (68-80) are observed further south where there is virtually no vertical uplift. Rainfall also plays a clear role as demonstrated by high rainfall on the west coast which causes lower riverine d234U when alpha-recoil mobilised 234U is quickly washed away. Both the U concentration and d234U are also altered by the lacustrine processes, particularly where glacial silt is present. Observed changes of d234U with time have been linked to past climate in a number of speleothem records. This study provides some support for the use of d234U as a proxy for rainfall, but also shows that d234U is extremely dependent on the rate of physical erosion.

V51C-0307 0830h POSTER

Do $(^{234}U)/(^{238}U)_o$ Variations in Speleothems Record Paleohydrologic Flux?

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Analysis of U-series disequilibria in speleothems not only provides a means of accurate chronology but also a record of $(^{234}U)/(^{238}U)$ variations in the source groundwaters through time. We present high precision TIMS data from speleothems and drip waters from Fogelpole Cave in Southern Illinois and suggest that

$(^{234}U)/(^{238}U)_o$ in drip waters is controlled by two parameters, paleohydrologic flux and the oxidation state of the waters. For a 65 cm long stalagmite, concordant ^{238}U-^{234}U-^{230}Th and ^{235}U-^{231}Pa ages for 5 samples indicate accurate chronology, and U concentrations remain high and constant around 50 ppm. As growth rate decreases from 230 to 3 mm/yr, $(^{234}U)/(^{238}U)_o$ decreases from 0.94 to 0.78. This differs from most speleothems globally that have $(^{234}U)/(^{238}U)_o > 1$ which increases with decreasing growth rate. A generalized observation is that $(^{234}U)/(^{238}U)_o$ deviates farther from secular equilibrium at slower growth rates and approaches 1 at faster grow rates. A explanation for this is that $(^{234}U)/(^{238}U)_o$ is dependent on fluid flow rates, possibly due to the role of 24 day half-life ^{234}Th during reactive transport. If so, $(^{234}U)/(^{238}U)_o$ could be an indicator of paleohydrologic flux. At the same time, we observe an inverse relationship between $(^{234}U)/(^{238}U)_o$ and U concentation for all of the speleothems (5) from Fogelpole cave following the systematics of groundwaters globally. Four U rich samples have ^{234}U deficits and 1 sample poorer in U has slight ^{234}U excess As interpreted previously, this probably indicates that changes in U redox chemistry also affect $(^{234}U)/(^{238}U)_o$.

V51C-0308 0830h POSTER

Soil ^{234}U-^{238}U and the Potential Use of U-series Disequilibrium as a Weathering Tracer

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Variations in $^{234}U/^{238}U$ activity ratios may be used to constrain weathering sources, weathering fluxes, soil development timescales, and water flowpaths in a watershed. The use of uranium-series disequilibria as a tracer and chronometer, however, hinges on a full understanding of the processes governing the behavior of uranium in the whole system, especially the soil environment. We present data on uranium concentrations and $^{234}U/^{238}U$ activity ratios in bedrock and soil mineral samples, soil porewaters, and groundwater and streamwater samples from a previously well-characterized watershed in Puerto Rico, in order to constrain the specific chemical processes controlling the supply of ^{234}U and ^{238}U isotopes to the streamwater. The study site, the Rio Icacos watershed in the Luquillo Mountains, has the highest documented chemical weathering rate of granitoid rocks on the Earth's surface. Trace element ratios and $^{87}Sr/^{86}Sr$ ratios are also used along with the U-series data to elucidate the weathering history. Sequential soil extraction data in combination with XRD and isotopic ICP-MS analyses provide information on the role of Fe-oxide and organic matter sorption on the behavior of uranium in the soil. Temporal sampling of streamwaters through varying discharge allows us to connect specific isotopic signatures to flow-paths through different layers of the weathering profile. A detailed account of the weathering mass balances in the watershed is available to substantiate interpretation of the U-series data. The project investigates the potential of U-series data to date weathering profiles, trace weathering products in surface waters, and calculate weathering mass balances.

V51C-0309 0830h POSTER

Uranyl Incorporation in Organic-Bearing Soil Calcite

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Phosphor imaging and fission track maps reveal a close correlation between uranium and organic-rich calcite that lines roots in an ancient caliche soil. Concordant U-Pb ages show that this uranium has not been mobilized since the soil calcite formed 298 $\pm$ 1 Ma ago. Luminescence spectroscopic analysis of the organic-rich calcite demonstrates that uranium is present in the oxidized state. More or less comparable luminescence spectra were collected using a CW lamp at room temperature and at liquid nitrogen (LN2) temperature. Spectra for inorganic U species are generally greatly enhanced at liquid nitrogen temperatures over room temperature and thus the similarity may suggest that the U is bound to organic matter. UV-excitation Raman spectroscopy of the calcite samples reveals a vibrational signature that is, in addition to the calcite peaks, essentially identical to that of sodium humate, acquired under similar conditions and consistent with those reported previously for humate substances. Since these spectra are dominated by the carbon backbone structure, the persistence of a carbon backbone structure is noted, but persistence of the ligating functional groups cannot be proven directly. We suggest that this sample records a snapshot of the process of uranium complexation with organic acids in natural systems. In our model organic acids with active functional groups that complex uranyl are sorbed onto the calcite surface and then incorporated as humate into the mineral with further calcite precipitation. Further, the uranyl complex is preserved through near-surface reducing conditions and temperatures to the conditions associated with 2700 meters burial depths. These combined observations suggest that the encapsulating calcite not only prevents reduction of uranium in the surface environment, but also inhibits the breakdown of the humate with burial. Due to the long time scale of immobilization of uranium, evidenced by the age of the calcite, this study has profound implications for understanding sampling for U-series and U-Pb dating of carbonates as well as for developing strategies for nuclear waste management. This study also has implications for any other deposits where uranium is associated with organic matter.

V51C-0310 0830h POSTER

Vadose Zone Weathering Rates Inferred from U-Series Disequilibrium

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The U-series isotope system can be used to quantify reaction rates in aquifers and thick vadose zone environments. The approach is based on the α-recoil of ^{234}Th atoms across grain boundaries, which enriches the pore fluid in ^{234}U. Dissolution of the solid phase releases mainly 238U to the pore fluid, so that the $^{234}U/^{238}U$ activity ratio of the pore fluid is a measure of the local ratio of the dissolution U flux to the α-recoil flux. The interpretation of U-series disequilibrium in weathering environments depends on the α-recoil flux, which is highly dependent on both the distribution of U and the grain size distribution of the soil. The recoil length of the ^{234}Th atom in a silicate is approximately 700 $\AA$, therefore the fine-grained material, with a greater surface area to volume ratio, contributes a significant amount of the ^{234}U to the porewater. As a result, estimates of the recoil flux based on the mean grain size may under predict the supply of ^{234}U by over an order of magnitude. In order to quantify the reaction rate, this recoil flux must be accurately measured by consideration of the recoil contribution of the fine-grained material, despite the fact that it may only comprise a small fraction of the total mass of the sediment. U concentrations and high precision isotope measurements ($^{234}U/^{238}U$) of pore fluids, mineral separates, and grain size intervals are used to constrain reaction rates for a 70 m vadose zone core from eastern Washington State. The pore water $^{234}U/^{238}U$ activity ratios range from 1.04 to 1.20 in the pore fluids, and from 0.94 to 1.0 in the various size fractions. Data from the solid phases is used to construct a predictive model for α-recoil flux in heterogeneous soil. The calculated recoil loss, which considers each grain size interval, is up to 7 times greater than for a geometric prediction based on the mean grain size. The measured $^{234}U/^{238}U$ ratios for the vadose zone, in conjunction with the estimates for the a-recoil flux, yield weathering rates of approximately $10^{-6.4}$ yr^{-1}, which agree with estimates derived from measurements in granitic soils that are based on mineral abundances and soil age. The data suggest that recoil loss from the fine-grained size fractions in a heterogeneous soil can have a significant impact on the interpretation of U isotopic data.

V51C-0311 0830h POSTER

U-Series in Large River Basins : Contraints on Processes and Timescales of Physical and Chemical Erosion

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It has become increasingly clear that erosion is a complex function of climate, relief and lithology. All these parameters impact on the rates of chemical and physical erosion; yet, it is largely unresolved how fast the system respond to these forcing functions at the scale of a watershed. To address these questions, we have initiated over the past few years, the study of U-series nuclides (^{238}U-^{234}U-^{230}Th-^{226}Ra) in about 50 rivers of variable sizes (Mackenzie, Amazon, Narmada and Tapti, India). We have also measured complementary trace, major elements and radiogenic isotope data. In order to be able to constrain mass balances properly, we have analyzed both dissolved and suspended loads and, in some cases, bed sediments. The suspended load and bedload are in most cases depleted in the more mobile nuclides (^{238}U-^{234}U-^{226}Ra) that are thought to be leached during chemical weathering relative to the more immobile ^{230}Th. By comparison, the dissolved load is enriched in the mobile nuclides. ($^{238}U/^{230}Th$) and ($^{226}Ra/^{230}Th$) in the dissolved load correlate positively. One must note that there is no correlation between ($^{238}U/^{230}Th$) and ($^{226}Ra/^{230}Th$) in the suspended load, which indicates that the timescale of particle weathering and transport must be greater than the half-life of ^{226}Ra (1600 a). If one makes the hypothesis that the bedrock was initially in secular equilibrium, the relative fraction of U-series nuclides transported in rivers as a result of chemical (dissolved load) or physical erosion (suspended and bed loads) can be estimated. An important result of these calculations is that erosion does not always operate at steady-state as inferred by geomorphologists. By comparing the present and past rate of denudation derived from U-series, we can infer constraints about the evolution of erosion in the watershed. In Andean rivers, the denudation rate would tend to destroy currently existing soils and the residence time of particles in soils is short. Simple models for the release of nuclides using first-order release rates provide rough estimates of the timescale of weathering for the suspended load. This timescale is short (a few ka to 10-20 ka) for mountain rivers (Andes) and recently glaciated areas (Mackenzie) and commensurate with the half life of ^{230}Th (or greater) for shield areas (lowlands of the Amazon basin) or rivers flowing on the Deccan trap (Narmada, Tapti). Bed sand transport times are in general greater than for suspended load (tens of ka).

V51C-0312 0830h POSTER

Uranium-Series Geochronology of Hydrothermal Deposits, Dixie Valley, Nevada

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Uranium-series dating of hydrothermal calcite, opal and quartz has been undertaken to help understand fluid transport and the timing of hydrothermal events associated with faulting in the Dixie Valley region. The Dixie Valley active geothermal system is located 160 km NE of Fallon in west-central Nevada within the Basin and Range tectonic province, and is fed by geothermal fluids arising from about 3000m depth. The fluid rises through faults and fractures associated with extension of the Stillwater fault system. A total of 14 samples comprised of travertine, or interlayered calcite, opal and quartz, were obtained from four deposits (groups 1-3, 5) along the valley. Samples were purified by handpicking, and where applicable, were separated into calcite, quartz or opal-rich fractions (20 separates in total). Samples were digested, spiked, and purified

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following standard methods. Uranium and some thorium measurements were obtained using a Micromass Sector54 TIMS equipped with a WARP filter. Many of the thorium measurements were obtained with a GV Isoprobe MC-ICP in the "soft extract" mode using the Cetac Aridus nebulizer. The Isoprobe provided greatly improved sensitivity and accuracy relative to the TIMS instrument. Uranium concentrations in quartz, opal and calcite separates range from 0.001 ppm to 1.227 ppm, and Th from 0.0001 to 3.278 ppm. Ages were obtained from isochron plots of calcite-opal/quartz pairs, or from a given group of samples assumed to share the same initial or detrital $^{230}Th/^{238}U$ and $^{234}U/^{238}U$. The resulting preliminary ages are: Group 1: 5 ka; Group 2: 4 ka and 5 ka; Group 3: 97 ka; Group 5: 4.7 ka and 0.4 ka. The relatively young ages close to 5 ka for most samples from Groups 1, 2, and 5 are consistent with expectations based on the presence of active fumaroles that indicate a current heat source, as well as geologic observations for recent faulting that has provided conduits for fluid flow. The older age of 97 ka from group 3 travertine deposit is also consistent with expectations, as cold seeps and the absence of fumaroles indicate a lesser degree hydrothermal activity. These results show that U-series chronology is an important tool for understanding the longevity of hydrothermal systems and the time-scales of fluid-flow in the crust.

V51D MCC: Level 1 Friday 0830h

Medical Mineralogy Posters *(joint with MR)*

Presiding: **G S Plumlee,** U.S. Geological Survey

V51D-0313 0830h POSTER

Minerals, Tobacco and Smoking-Related Disease

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As much as 8% (by dry weight) of commercial tobacco is mineral, and the view that minerals are inert, playing no more than a passive role in smoking-related disease, is challenged. An inventory of minerals in tobacco is presented and an interpretation of their sources given. Using elemental abundances the relative contributions of natural and anthropogenic sources to the commercial product is quantitatively modelled relative to average crustal abundances. A framework is presented for investigating the potential ways in which minerals with, or acquire, toxic properties behave in the smoking environment. In order to represent a potential hazard any mineral (or mineral reaction product) with suspected toxic properties must partition into smoke and be respirable. For inhalation a significant proportion of the particles must be smaller than 10 microns. Three categories of potential hazard are recognised: 1. Minerals with intrinsic toxic properties. Quartz can amount to 1% or more in some cigarettes and is defined as a human carcinogen by the IARC. It is not likely to represent a hazard as its grain size is probably too coarse to be respirable. However talc, also a Type 1 carcinogen when it is contaminated with asbestos, is a common constituent of cigarette paper and may be of respirable size. Some other minerals also fall into this category. 2. Minerals that generate toxic products on combustion. Examples are the biominerals calcium oxalate monohydrate (whewellite) and dihydrate (weddellite), which amount to about 5 wt% of popular UK brands. These minerals decompose at tobacco combustion temperatures yielding large quantities of carbon monoxide. A substantial fraction of the CO budget of UK cigarettes may derive from this source. 3. Minerals that acquire toxic properties on combustion. Little is known about free radical generation on mineral surfaces during tobacco combustion, but the devolatilisation of calcic phases (carbonates and oxalates) creates oxide particles with surfaces highly adsorbent to polycyclic aromatic hydrocarbons (PAH). Calcic mineral particles are two orders of magnitude more abundant in smokers' lungs compared with non-smoking controls in residents of Vancouver. Such particles may thus be potential agents for the delivery of PAH carcinogens, including benzo(a)pyrene, to the lungs. None of the potential hazards listed above has yet been properly evaluated.

V51D-0314 0830h POSTER

Respiratory Health Effects of Volcanic Ash - a new Approach

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Attempts to characterise the toxicity of volcanic ash have focused on the presence of the crystalline silica polymorph cristobalite, which is known to cause silicosis and lung cancer in industrial settings. Within the lung, it is the surface of the particles which will react with endogenous molecules. Free radicals, produced on particle surfaces, can react with DNA and other cellular components, instigating a chain of toxic events. For the first time, the ability of volcanic ash to form free radicals has been assessed using Electron Paramagnetic Resonance techniques specific to the hydroxyl radical. Respirable (< 4 microns) crystalline silica, separated from volcanic ash from the Soufriere Hills volcano, Montserrat, West Indies, did not produce hydroxyl free radicals or surface radicals. However, the ash, itself, generated up to 3 times more hydroxyl radicals than a quartz of known toxicity. The cause of the reactivity is reduced iron on the surface of iron-rich minerals such as amphiboles and pyroxenes. Fresh volcanic ash generates more free radicals than weathered volcanic ash which will have oxidised (and leached away) surface iron. These results have implications for volcanic health hazard research as it was previously assumed that volcanoes which did not produce respirable crystalline silica presented a lesser respiratory health hazard. The International Volcanic Health Hazard Network (IVHHN) promotes research into the health effects of volcanic emissions. Under the auspices of IVHHN, volcanic ash samples from volcanoes world-wide are being analysed for surface reactivity, grain-size distribution and composition to form a comprehensive database for use by volcano observatories, emergency managers, medical practitioners and researchers. The results will highlight volcanoes which have the potential to cause a respiratory health hazard through generation of iron-catalysed free radicals, as well as more conventional markers such as concentration of respirable particles. At the onset of new eruptions, the database will be used to aid the rapid assessment of health hazard from volcanic ash.

URL: http://eis.bris.ac.uk/~glcjh/ivhhn

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Mineralogical Studies Related to Endemic Diseases in Rural P. R. China

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Domestic combustion of coal for heating and cooking is mostly confined to the world's developing countries and probably involves about 1 billion persons in China, India, Indonesia, and Africa. Various endemic diseases affecting millions of people involving arsenic, selenium, and fluorine poisoning have been associated with domestic coal combustion in rural China. We have investigated the relationship between mineralized coals (and stone coals) and disease occurrences in Guizhou and Hubei Provinces. The mineralogy of the coals has been studied by a wide variety of techniques, including optical petrography, scanning electron microscopy, electron microprobe analysis, ion probe, Synchrotron XANES-EXAFS, and Raman spectroscopy. Arsenic enrichment (up to 3 weight percent) in Upper Permian Longtan Formation coals, southwestern Guizhou Province, occurs in both 3+ and 5+ valence states. Arsenic occurs in arsenopyrite, pyrite, Al-phosphate, scorodite, Fe-oxides, and as an organically-bound species. Fluorine poisoning, much more widespread than arsenic-poisoning, is related to burning F-rich coals and F-rich clays as admixtures. Mineralogical and chemical analysis suggests that the clays contain the fluorine probably substituting for the hydroxyl group. Localized selenium poisoning in Hubei Province is related to Se-rich stone coals. The selenium occurs as a native element and in rare mandarinoite. In these three cases, knowledge of the paragenesis and mineralogy of the element enrichment in coal was vital to help understand and mitigate the endemic diseases. For the situation concerning arsenic and selenium poisoning, suspect coals have been identified and mining from these deposits has been curtailed. Fluorine has been a much more difficult problem for the local public health officials as both the coal and clay in the burning admixture can contain high fluorine. Regional geochemical and mineralogical studies will help to define coal and clay with low fluorine, suitable for domestic use.

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The Toxicological Geochemistry of Dusts, Soils, and Other Earth Materials: Insights From In Vitro Physiologically-based Geochemical Leach Tests

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Exposure to mineral dusts, soils, and other earth materials results in chemical reactions between the materials and different body fluids that include, depending upon the exposure route, lung fluids, gastrointestinal fluids, and perspiration. In vitro physiologically-based geochemical leach tests provide useful insights into these chemical reactions and their potential toxicological implications. We have conducted such leach tests on a variety of earth materials, including asbestos, volcanic ash, dusts from dry lake beds, mine wastes, wastes left from the roasting of mercury ores, mineral processing wastes, coal dusts and coal fly ash, various soils, and complex dusts generated by the World Trade Center collapse. Size-fractionated samples of earth materials that have been well-characterized mineralogically and chemically are reacted at body temperature (37 C) for periods from 2 hours up to multiple days with various proportions of simulated lung, gastric, intestinal, and/or plasma-based fluids. Results indicate that different earth materials may have quite different solubility and dissolution behavior in vivo, depending upon a) the mineralogic makeup of the material, and b) the exposure route. For example, biodurable minerals such as asbestos and volcanic ash particles, whose health effects result because they dissolve very slowly in vivo, bleed off low levels of trace metals into the simulated lung fluids; these include metals such as Fe and Cr that are suspected by health scientists of contributing to the generation of reactive oxygen species and resulting DNA damage in vivo. In contrast, dry lake bed dusts and concrete-rich dusts are highly alkaline and bioreactive, and cause substantial pH increases and other chemical changes in the simulated body fluids. Many of the earth materials tested contain a variety of metals that can be quite soluble (bioaccessible), depending upon the material and the simulated body fluid composition. For example, due to their acidic pH and high chloride concentrations, simulated gastric fluids are most efficient at solubilizing metals such as Hg, Pb, Zn, and others that form strong chloride complexes; although these metals tend to partially reprecipitate in the near-neutral simulated intestinal fluids, complexes with organic ligands (i.e., amino and carboxylic acids) enhance their solubility. These metals are also quite soluble in near-neutral, protein-rich plasma-based fluids because they form strong complexes with the proteins. In contrast, metalloids that form oxyanion species (such as As, Cr, Mo, W) are commonly more soluble in near-neutral pH simulated lung fluids than in simulated gastric fluids.

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Structure of Carbonate Apatites Synthesized at 2-4 GPa

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Type A carbonate apatite (CAp), type A and B carbonated apatites, and complex type A-B CAp have been synthesized at 2-4 GPa and 1400-1500°C in a piston cylinder apparatus, and the accommodation of the carbonate ion studied at NTP using FTIR spectroscopy and X-ray structure analysis. Apatite compositions approximate to $Ca_{10}(PO_4)_{6-y}(CO_3)_{x+(3/2)y}(OH)_{2-2x}$, x = 0.0-0.7, y = 0.0-0.6. A new space group (P-3) and structure are reported for type A CAp with x = 0.5-1.0, y = 0.0. The type A carbonate ion is ordered along the apatite channel at z = 0.5; two of its oxygen atoms are close to the c-axis, and the plane of the ion is canted about 12°. This is the "closed" channel configuration,