# The adsorption of As onto hydroxy-Fe-montmorillonite complexes

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**Abstract**

Arsenate ions have high affinity for soluble hydroxy-Fe species and for Fe-oxyhydroxide precipitates. The hydrolysis of Fe(III) and the growth of initially precipitated Fe(III) phases is, in turn, strongly affected by montmorillonite. In this paper, the adsorption of As onto various hydroxy-Fe-montmorillonite complexes was studied. Three types of samples were prepared by mixing montmorillonite, hydroxy-Fe and arsenate in different sequences: 1. Montmorillonite+hydroxy-Fe before addition of arsenate; 2. Hydroxy-Fe+arsenate before addition of montmorillonite; 3. Montmorillonite+arsenate before addition of hydroxy-Fe.

For each system, the effects of pH, ionic strength, temperature, initial Fe concentration, adsorption duration and initial As concentration on the overall uptake of As by hydroxy-Fe-montmorillonite complexes were studied. Results show that the uptake of As increases with increasing pH, temperature, initial Fe concentration and adsorption duration and decreases with increasing ionic strength and with initial As concentration. These effects occur to differing extents in the three systems. The variation of As uptake by the hydroxy-Fe-montmorillonite complexes in the pH range under investigation is opposite to that previously reported for systems in the absence of montmorillonite. It is similar to that reported elsewhere for the pure montmorillonite system in the absence of hydroxy-Fe. The marked influence of ionic strength on the As uptake of hydroxy-Fe-montmorillonite complexes indicates that complexation by As in the outer coordination shell is likely to be important. This is quite different from that of As adsorption on the surface of Fe-oxyhydroxides and montmorillonite in which inner-sphere adsorption dominates. Under all experimental conditions, hydroxy-Fe-montmorillonite complexes displayed very strong affinity for As with system (2) having the highest As adsorption capacity and system (1) the lowest. The authors attribute this to the difference in mixing sequences adopted. This resulted in more hydroxy-Fe (the main adsorbent for As) being adsorbed onto montmorillonite for system (1) before the hydroxy-Fe complex is able to adsorb As, than is the case for systems (3) and (2). The mineralogical constituents of hydroxy-Fe-montmorillonite complexes and their spatial correlation after As adsorption were studied by powder x-ray diffraction and transmission electron microscopy. Two Fe-oxyhydroxide particles of different shapes were observed: (i) near-equant grains of less than 100nm in size, aggregated in bigger agglomerates of varying size between the montmorillonite grains; (ii) fibrous particles 1-2µm long accumulated around montmorillonites. The formation of these Fe grains and the role they played in the adsorption of As are the subject of further study.

# U-Pb SHRIMP-dating of zircon domains from xenoliths of the Rio Grande Rift (Kilbourne Hole): implications for the timing of mantle events

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The Kilbourne Hole (KH), New Mexico, southern Rio Grande Rift (RGR) is one of the several maars associated with basanitic flows within the Quaternary Potrillo field. A variety of upper mantle- and lower crustal xenoliths occur in the ejecta of these 80±10 ka old basanites. They record information on the continental rift-related mantle. To constrain the timing and nature of mantle events and examine whether they correlate with known events in the continental crust, we dated zircons by SHRIMP II at ANU (Canberra) and GSC (Ottawa) from four different types of xenoliths of the KH: peridotites (PD), pyroxenites (PY), felsic granulites (FG) and two-pyroxene mafic granulites (MG). Zircons have variable shapes, cathodoluminescence patterns and ages: One inherited Archean (3390±75 Ma; 1_) zircon domain in the FG and four inherited Proterozoic zircons and zircon domains of ca. 1610-1870 Ma were dated in the PD, the PY, and the FG. These ages correlate well with those of the base of the crust in the southern RGR accreted to the N' American continental margin between 1.6 to 1.8 Ga. Zircons of Phanerozoic ages are as follows: (a) *Devonian-Triassic*: a series of ages (possibly discordant) between ca. 373 and ca. 235 Ma from oscillatory zoned zircon crystals of the MG are probably associated with the Ouachita orogen. A ca. 208 Ma old oscillatory zoned zircon in the PD possibly formed during an extension-related mantle melting episode. (b) *Upper Cretaceous*: a weighted mean age at 73.5±2.9 Ma (4 spots; error at 95% c.l.) from a euhedral, oscillatory zoned zircon of the PD reflects mantle melting episodes probably related to Laramide subduction/ accretion events and assoc-iated 75-60 Ma old continental margin volcanism. (c) *Upper Eocene-Lower Oligocene*: ages at ca. 35 Ma from oscillatory zoned zircon domains of the PD and the FG and a bright homogeneous rim domain at 26.4±2.6 Ma (1_) from the FG seem to be correlated with both pre-rift magmatic activity and an early stage of extension at ca. 26 Ma. This event may have triggered metamorphic recrystall-ization along zircon rims caused by lower crustal heat input during underplating of mafic magmas. It is worth mentioning that a weighted mean age at 32.2±1.4 Ma (5 spots; error at 95% c.l.) was also obtained from oscillatory zoned zircons of a peridotite mantle xenolith of the Camargo basalt field, Chihuahua, Mexico. (d) Finally, very young ages at ca. 5.5 Ma were obtained from the PD and even younger, at ca. 2.7 Ma, from the FG (oscillatory zoned domain). These very young zircons must be connected with anorogenic and extension-related partial mantle melting that led to the formation of the RGR. An implication is that, for lack of time, at least these youngest zircons cannot have been mixed into the mantle by subduction of eroded, very young continental sources.