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Authors:	Furrer, Gerhard Phillips, Brian L. Ulrich, Kai-Uwe Pöthig, Rosemarie Casey, William H.
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The Origin of Aluminum Flocs in Polluted Streams

About 240,000 square kilometers of Earth's surface is disrupted by mining, which creates watersheds that are polluted by acidity, aluminum, and heavy metals. Mixing of acidic effluent from old mines and acidic soils into waters with a higher pH causes precipitation of amorphous aluminum oxyhydroxide flocs that move in streams as suspended solids and transport adsorbed contaminants. On the basis of samples from nine streams, we show that these flocs probably form from aggregation of the e-Keggin polyoxocation $AlO_4\ Al_{12}(OH)_{24}(H_2O)^{7,\text{ sub }12}$ +>(aq) (Al_{13}), because all of the flocs contain distinct $Al(O)_4$ centers similar to that of the Al_{13} nanocluster.

In studies of the aluminum geochemistry of acid mine drainage (1,2), solids were identified that precipitate at 4.2 < pH < 4.9 as either x-ray—amorphous $Al(OH)_3$ or microcrystalline gibbsite. These flocs are fluffy (Fig. 1) and form as acidic effluent enriched in dissolved aluminum mixes with near-neutral surface water. A similar phenomenon occurs in watersheds where the load of acid rain critically exceeds the buffering capacity of the soil and parent rock (3). It is thought (4) that the flocs form by aggregation of monomeric aluminum complexes into a $Al_6(OH)_{12}(H_2O)^{12,\text{ sub }6+}$ multimer that is structurally similar to dioctahedral sheets of gibbsite. Dissolved $Al_6(OH)_{12}(H_2O)^{12,\text{ sub }6+}$, however, has never been detected, and this model has been challenged (5).

Here we propose an alternative explanation. We examined flocs from nine polluted streams in Germany and California (Table 1) (table S1 and figs. S2 to S4) with ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, which resolves aluminum atoms with different coordination environments. The ^{27}Al NMR spectra of all field samples exhibit signals near +63 and +35 parts per million (ppm), which indicate the presence of substantial amounts of aluminum in tetrahedral form [$Al(O)_4$] and in coordination to five oxygen atoms [$Al(O)_5$] (6), in addition to the dominating $Al(O)_6$ peak near +7 ppm. Because the spectra of all samples were similar, we selected three samples to show the range in relative intensities (Fig. 2A). The first and last samples (Fig. 2A, top and bottom) have the most and least amounts of $Al(O)_4$, respectively. The second sample (Fig. 2A, middle) is typical of the seven other samples. The concentration of $Al(O)_4$ reached ˜7% of the total Al(III) (Fig. 2A, top). The signal near +63 ppm cannot be attributed to clay, such as illite or smectite, which would yield a peak near +70 ppm (7). Examination of the field samples by x-ray diffraction did not show any crystalline phase other than traces of quartz. Similar ^{27}Al NMR spectra have been reported from flocs in organic-rich lake waters that are also rich in aluminum (8).

The stable $Al(OH)_3$ minerals (gibbsite, bayerite) contain only sheets of edge-linked $Al(O)_6$, leading us to the hypothesis that the high $Al(O)_4$ concentrations in the stream flocs are structural remnants of dissolved aluminum molecules. There are only three species in acidic aqueous solutions that have $Al(O)_4$: the mononuclear $Al(OH)^{4,\ \text{sub \−}}$ (aq) and the polyoxocations $AlO_4Al_{12}(OH)_{24}(H_2O)^{12,\ \text{sub } 7+}$(aq) ($Al_{13}$), which has an e-Keggin-like structure (Fig. 3), and $(AlO_4)_2Al_{28}(OH)_{56}(H_2O)^{18+,\ \text{sub } 24}$ (aq) (Al_{30}), the structure of which has recently been resolved (9,10). This molecule can be synthesized within hours only at elevated temperature (95°C), so it is unlikely to form in streams.

Under equilibrium conditions, the Al_{13} polyoxocation can account for much more of the total $Al(O)_4$ in the polluted waters than the monomeric $Al(OH)^{\text{\−, Sub } 4}$(aq) complex. With accepted equilibrium constants (11,12), Al_{13} is predicted to form at total dissolved aluminum concentrations (SAl) of more than 20 µM at $pH > 5$. The filtered waters from our field sites (Table 1) exhibit $20\ \mu M < SAl < 180\ \mu M$ and $5.0 < pH < 5.5$. At metastable equilibrium, a solution with $pH = 5.0$ and $SAl = 100\ \mu M$ contains 78% of SAl in the form of Al_{13}, whereas $Al(OH)^{\text{\−, sub } 4}$ (aq) makes up only 0.01%. The other 22% are distributed almost equally between the monomeric species Al^{3+}(aq), $Al(OH)^{2+}$(aq), and $Al(OH)^{+,\ \text{sub } 2}$ (aq). In such a solution, $Al(O)_4$ amounts to at least 6% of Al, and the amount of $Al(O)_4$ incorporated in Al_{13} is 600 times that in $Al(OH)^{\text{\−, sub } 4}$(aq). Although equilibrium calculations give no information about disequilibrium pathways, they indicate that Al_{13} is potentially abundant and that virtually all aluminum-rich acid drainage waters pass through the Al_{13} metastability field during mixing with pristine surface waters. Because Al_{13} forms quickly in aqueous solution, dis-equilibrium caused by poor mixing of the acidic and basic solutions will result in even greater concentrations of Al_{13} than indicated by the calculations.

Because the Al_{13} molecule is sufficiently unreactive once formed, it can retain vestigial $Al(O)_4$ if polymerized rapidly into a solid as the pH rises and causes bound water ligands to deprotonate. At conditions typical for polluted streams, decomposition of Al_{13} molecules takes hundreds of hours (e.g., half-life ˜ 580 hours at pH = 5 and 283 K) (13), as does the exchange of structural oxygens with bulk solution (14); yet it is evident that Al_{13} forms within minutes, which is the minimum time necessary to collect an ^{27}Al NMR spectrum.

We synthesized flocs with aluminum solutions under conditions similar to those encountered during mixing of acidic mine waters with neutral surface waters. In all cases, the resulting gels contained substantial amounts of $Al(O)_4$ and $Al(O)_5$, even when the titrations were conducted rapidly and at low temperature (Fig. 2B, bottom). The supernatant solution usually contained detectable Al_{13}, which is evident in spectra of wet gels.

We repeated the experiments with solutions that do not contain $Al(OH)^{\text{\−, sub } 4}$(aq) to determine whether Al_{13} can account for $Al(O)_4$ observed in the field samples. We performed experiments with monospecific Al_{13} solutions and with monospecific $GaO_4Al_{12}(OH)_{24}(H_2O)^{7+,\ \text{sub } 12}$(aq) ($GaAl_{12}$) solutions. This $GaAl_{12}$ molecule has gallium substituted exclusively into the central tetrahedral site (15) and no $Al(O)_4$. As expected, if Al_{13} was the source of $Al(O)_4$ in the gel, we observed retention of $Al(O)_4$ when Al_{13} molecules were condensed in solution, but we did not observe $Al(O)_4$ when $GaAl_{12}$ was aggregated.

This experiment shows that the coordination of the tetrahedral center is retained in the solid when the molecules are condensed into a gel. Accordingly, the ^{71}Ga MAS NMR spectrum (9.4 T) of the same gel gave a relatively broad peak for tetrahedrally coordinated gallium centered near 122 ppm (15). However, the gels obtained from monospecific Al_{13} solutions do not contain a distinct signal for $Al(O)_5$, which suggests that these sites form by interaction of Al_{13} with monomeric aluminum complexes, which were excluded from the solutions.

Because Al_{13} formation is suppressed in the presence of high sulfate concentrations (16), we also conducted several experiments simulating the slow dilution of acid mine water, containing 0.1 M $AlCl_3$ and 0 to 0.6 M sulfate, into water buffered by marble chips. At all SSO_4/SAl(III) ratios, we found substantial amounts of $Al(O)_4$ and $Al(O)_5$ in the flocs after separation from the marble chips.

A close genetic link between Al_{13} and solid aluminum hydroxides has been postulated (17,18). However, the Al_{13} species is difficult to observe in nature because the pH window between formation and aggregation is small and because mixing of polluted and unpolluted waters is usually rapid and episodic. All of our results support the hypothesis that the aluminum flocs commonly found in polluted streams originate mainly from condensation of

Al_{13} molecules that form rapidly and then aggregate as pH of the effluent increases to more than 5.

These results are important because Al_{13} is phytotoxic (5,19) and is probably responsible for the decline of fish populations in rivers polluted by mine drainage and acid rain (20). Its longevity and chemical affinity for heavy-metal cations, such as Pb^{2+}, Cu^{2+}, or Zn^{2+}(table S1) (21), suggest that dissolved Al_{13} and suspended aluminum flocs can transport metals downstream over considerable distances.

Supporting Online Material

www.sciencemag.org/cgi/content/full/297/5590/2245/DC1

Figs. S2 to S4

Table S1

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Table 1. Characterization of the selected field samples of representative aluminum oxyhydroxide flocs, collected from 1996 to 2001. Some samples were centrifuged immediately after collection and then dried under ambient conditions. Other samples (e.g., those from Spenceville) were analyzed both as a wet paste and as an air-dried gel. The aluminum concentrations were measured in the 0.45 µm-filtered water samples from the mixing zones. For the sample shown in Fig. 2A, middle, values are not available from direct in situ measurements in the mixing zone because the acid mine effluent ($pH = 2.3$; $1 \text{ mM} < SAl < 15 \text{ mM}$) enters the pristine stream water [$pH = 7.7$; $SAl <$ detection limit (d.l.)] from the hyporheic zone.

Legend for Chart:

A - Sample spectrum
B - Geographic region
C - Geology
D - Vegetation
E - Type of pollution
F - Sampling date
G - pH in mixing zone
H - Aluminum concentration

A

B

C

D

E

F

G

H

Fig. 2A, top

East Thuringian, Slate Mountains, Germany
Carboniferous blue slate
Mixed forest

Acid mine drainage

22 May 1998

5.0 to 6.5

20 to 180 µM

Fig. 2A, middle

Spenceville, Yuba County, California

Metavolcanic rocks

Mixed forest

Acid mine drainage

4 Jan 2001

–

0 to 16 mM

Fig. 2A, bottom

Ore Mountains, Saxony, Germany

Mica slate, gneisses

Spruce

Acid rain

25 Mar 1999
5.0 to 5.5
18 to 60 µM

GRAPH: Fig. 2. Selection of ^{27}Al MAS NMR spectra (28) of natural and synthetic aluminum oxyhydroxide gels. The prominent broad peaks near 0 ppm indicate $Al(O)_6$ environments. The signals near +60 and +35 ppm correspond to $Al(O)_4$ and $Al(O)_5$, respectively. The fractions of four- and five-coordinated aluminum are 1 to 7% for $Al(O)_4$ and 5 to 9% for $Al(O)_5$. The nature of $Al(O)_5$ is uncertain, but it may originate from $Al(O)_6$ because some samples exhibit total intensities for $Al(O)_4$ and $Al(O)_5$ that exceed 1/13 the stoichiometric $Al(O)_4$ fraction for Al_{13}. (A) Spectra of representative aluminum oxyhydroxide flocs from streams polluted by acid mine drainage in Germany (top) and in California (middle) and from the junction of a stream acidified by acid rain and a neutral stream in Germany (3) (bottom). The intensity of the $Al(O)_4$ signal in the top spectrum corresponds to 7(±1)% of the total aluminum. (B) Spectra of synthetic ftocs. No signals for $Al(O)_4$ or $Al(O)_5$ are observed if the gels are made from $GaAl_{12}$ molecules (29) (top). A peak near +60 ppm is seen in the spectra of a gel that is made by neutralizing an acidic aqueous solution containing dissolved Al_{13} as the only aluminum species (29) (middle). In addition to peaks for $Al(O)_4$ and $Al(O)_5$ in the solid phase, a sharp peak for Al_{13} in the fluid (bottom) was found in a get that was generated at ~5°C by instantaneous mixing of 0.2 M $AlCl_3$ and 0.48 M NaOH at equal volumes and analyzed within 30 min.

DIAGRAM: Fig. 3. The structure of the Al_{13} nanocluster in polyhedral presentation. The complex with the stoichiometry $AlO_4Al_{12}(OH)_{24}(H_2O)^{7+,\ sub\ 12}$ (aq) is composed of a central $Al(O)_4$ surrounded by 12 equivalent octahedrally coordinated aluminum atoms. Above pH ˜ 5.5, the charge of the polymer is lost by partial deprotonation of the 12 terminal water molecules (26). This triggers condensation of the nanoclusters into an x-ray—amorphous gel that eventually forms bayerite (27).

PHOTO (COLOR): Fig. 1. Aluminum oxyhydroxide floc on a streambed in Yuba County, California. The white aluminum oxyhydroxide floc overlies orange iron oxyhydroxide solids. Image width, ˜30 cm.

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6. Peak positions correspond to the data taken at 16.4T, which are less affected by second-order quadrupolar shifts. Peak positions at 9.4 T are 3 to 5 ppm more negative than those at 16.4 T. Assignment of the peak near +35 ppm to $Al(O)_5$ is based on the similarity of this chemical shift to those observed for crystalline phases that contain aluminum in coordination to five oxygens (22–25).

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28. *The ^{27}Al MAS NMR spectra were recorded in spring 2001 on a Chemagnetics CMX spectrometer at 104.25 MHz with single-pulse excitation, a pulse width of 1 µs, a relaxation delay of 0.1 s, and a digitizing rate of 500 kHz. The samples were placed in sealed rotors (4-mm outside diameter) and spun at 15 to 16 kHz. The spinning sidebands lie outside of the displayed spectral range. Synthetic gel samples were examined wet, immediately after centrifugation, and after drying under ambient conditions, but no substantial difference was noted in the ^{27}Al MAS NMR spectra. Additional spectra were taken several months later at 182.4 MHz with a Bruker Avance spectrometer and similar acquisition conditions, except that the spinning rate was 30 kHz. These spectra are much better resolved and confirmed the estimates of relative populations of coordination environments.*

29. *The solutions were prepared by metathetic dissolution of the corresponding Al_{13}- or $GaAl_{12}$-selenate crystals in the presence of dissolved $BaCl_2$ (14, 15, 26, 27).*

30. *Financial support came from the NSF, the U.S. Department of Energy, and Eidgenössische Technische Hochschule Zürich. Much of the work was conducted at University of California, Davis, during G.F.'s sabbatical leave. We thank A. P. Lee, P. Yu, and M. Ziliox for technical assistance; B. Wehrli and A. C. Johnson for valuable discussions; and R. Schulin and L. Paul for general support. Inductively coupled plasma—mass spectrometry analyses were provided by A. Birkefeld.*

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By Gerhard Furrer, Institute of Terrestrial Ecology, Eidgenö Technische hochschule Zürich, Grabenstrasse 3, CH-8952 Schlieren, Switzerland.; Brian L. Phillips, Department of Geosciences, State University of New York, Stony Brook, NY 11794-21000, USA.; Kai-Uwe Ulrich, Technical University of Dresden, Ecological Station Neunzehnhain, D-09514 Lengefeld, Germany.; Rosemarie Pöthig, Leibniz Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 310, D-12587 Berlin, Germany. and William H. Casey, Department of Land, Air, and Water Resources and Department of Geology, University of California, Davis, CA 95616, USA.

To whom correspondence should be addressed. E-mail: furrer@ito.umnv.ethz.ch (G.F.)

To whom correspondence should be addressed. E-mail: whcasey@ucdavis.edu (W.H.C.)
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Supplementary Material

(containing Table S1, Figure S2, Figure S3, and Figure S4)

Table S1. Chemical analyses (provided by Andreas Birkefeld, ETH Zurich) of seven air-dried samples of aluminum oxyhydroxide flocs found in German streams. Sample 3 (see Fig. 2A, top, for corresponding ^{27}Al MAS NMR spectrum) and Sample 5 are from the East Thuringian slate-mining area (for photographs see Figure S2). Sample 6 (^{27}Al MAS NMR spectrum: Fig. 2A, bottom) and Samples 7 - 10 are from the Ore Mountains in Saxony (photographs: see Figure S4). All concentrations are given in mg/kg. The digestion was conducted by dissolving 16 - 62 mg of solid floc into a solution containing 6 ml of 65% HNO_3, 2 ml of 30% H_2O_2 and 2 ml H_2O using a microwave digester at 180 ^{o}C for 25 min. The resulting solution was analyzed by ICP-MS. The analytical uncertainty is 15% or less. Sulfur analyses were conducted on three samples and range from 96 ppm to 28,700 ppm but we observe no systematic relation between chemical composition and the concentration of $Al(O)_4$ as determined by ^{27}Al NMR spectroscopy. In five samples the concentration of cadmium was not detectable (n.d.), i.e., smaller than 0.2 mg/kg.

Sample	Al	Fe	Cu	Cd	Ni	Co	Pb	Zn	Ca
3	190,000	3,630	3,600	0.23	73	5.6	24	1,300	1,540
5	189,000	1,540	1,320	n.d.	10	2.5	30	249	967
6	152,000	1,230	75	n.d.	7.4	1.4	36	96	272
7	148,000	1,340	56	n.d.	7.7	1.7	14	37	523
8	136,000	3,410	44	0.61	14	6.5	69	128	954
9	170,000	543	26	n.d.	5.5	1.9	118	69	1,660
10	156,000	9,090	82	n.d.	25	6.9	6.3	127	2,050

Figure S2. Stream beds in a mining area of the Slate Mountains, East Thuringia, Germany, covered with white flocs of aluminum oxyhydroxide (all three images). The ^{27}Al MAS NMR spectra show that these flocs contain high amounts of aluminum in tetrahedral coordination to oxygen atoms. Approximately 7% of the total aluminum is $Al(O)_4$, which means that 90% of the aluminum precipitates probably have evolved through the Keggin Al_{13} polyoxocation (for spectrum see Fig. 2A, top).

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Figure S3. Area with acid mine drainage in Spenceville, Yuba County, California. The effluent from the heavily acidic quarry pond (pH 2.3) (top left) enters the pristine stream water (pH 7) (right) from the hyporheic zone. The white aluminum oxyhydroxide flocs cover the stream bed in the mixing zone where the pH increases from approximately 3 to neutral values (bottom left) (^{27}Al MAS NMR spectrum: Fig. 2A, middle).

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Figure S4. A stream bed with white aluminum oxohydroxide flocs in the Ore Mountains, Saxony, Germany (left image; a close-up view is seen in the right image). Here, the load of acid rain exceeds by far the buffering capacity of the soil and the parent rock materials. A few meters further upstream the acidic surface water of a tributary stream that is enriched in dissolved aluminum merges with less acidic water from another stream. This mixing leads to the formation of the white flocs (^{27}Al MAS NMR spectrum: Fig. 2A, bottom).

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