29. In practice, for determining the fastest particles, we considered a new variable $D_i(t_0, \Delta t) = \max_{(t1,t2)}(|\vec{r}_i(t_1) - \vec{r}_i(t_2)|)$, where $t_0 \leq t_1, t_2 \leq t_0 + \Delta t$ and the subscript i is the particle index. This approach is similar to the definition used by previous authors (*12*) and is less sensitive to short-term particle motion. Most results are independent of the cutoff choice Δr^*.
30. F. P. Preparata and M. I. Shamos, *Computational Geometry* (Springer-Verlag, New York, 1985).
31. We computed a particle-averaged cluster size $\langle N_c \rangle \equiv [\Sigma n_c^2 P(n_c)/\Sigma n_c P(n_c)]$ rather than a cluster-averaged size $\Sigma n_c P(n_c)$. The latter measure gave similar results for ϕ and Δt dependence. We computed the expected cluster size for a random distribution of particles by taking the particle speeds at each time t_0, shuffling the particle speeds while keeping the particle positions fixed, and then computing the average cluster size, which is 2.2 ± 0.2 for our data.
32. We found the average particle has 14 nearest neighbors, similar to (*5*).
33. We thank S. C. Glotzer, P. N. Pusey, and P. N. Segrè for useful discussions. Supported by NSF (grants DMR-9631279, DMR-9971432) and NASA (grants NAG3-2058, NAG3-2284).

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Oxygen Isotopes and Emerald Trade Routes Since Antiquity

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Oxygen isotopic compositions of historical emerald-artifacts from the Gallo-Roman period to the 18th century indicate that during historical times, artisans worked emeralds originating from deposits supposedly discovered in the 20th century. In antiquity, Pakistani and Egyptian emeralds were traded by way of the Silk Route. Together with Austrian stones, they were the only source of gem-quality emeralds. Immediately after the discovery of the Colombian mines by Spaniards in the 16th century, a new trade route was established, first via Spain to Europe and India and then directly via the Philippines to India. Since then, Colombian emeralds have dominated the emerald trade, and most of the high-quality emeralds cut in the 18th century in India originated from Colombia.

Since Egyptian times, emeralds have played a key role in the history of civilizations, being a symbol of eternity and power and an artifact of legend (*1, 2*). Despite numerous studies based on historical records and on gemological characteristics such as color or mineral and fluid inclusions, the origin of most emeralds set in historical treasures remains uncertain or even enigmatic. This is the case for the so-called "old mine" emeralds (*1, 3*), which were distributed all over the world by Indian traders under the influence of the Bobur Moghul dynasty in the 16th century. It has been claimed that these famous emeralds came from old mines located somewhere in southeast Asia, although all the deposits in middle and far eastern Asia were officially discovered in the 20th century. Here we describe the results of an oxygen isotopic study of nine emeralds that have acquired an historical dimension and that were selected to cover a large period of time, from the Gallo-Roman epoch to the 18th century. The $^{18}O/^{16}O$ ratio of lattice oxygen in emeralds, added to more classical gemological characteristics, allow us to determine their provenance (*4*) and to document the evolution of emerald trade routes.

The oldest dated artifact we studied is a Gallo-Roman earring (property of the Muséum National d'Histoire Naturelle in Paris) made of gold and emerald and discovered in Miribel (Ain, France) in 1997. We also analyzed four emeralds from the treasury of the Nizam of Hyderabad (India) cut in the 18th century A.D. They are classically called "old mine" emeralds, and their historical record could go back to Alexander the Great (~300 B.C.) (*3*). We also studied the emerald from the Holy Crown of France (51.5 carats, property of the Muséum National d'Histoire Naturelle in Paris), which was set on the central jewel lily of the crown of France by Louis IX (Saint Louis), king of France between 1226 and 1270 A.D. Finally, we studied two large emeralds (property of the Muséum National d'Histoire Naturelle in Paris) that were used by Abbé Hauy, the founder of mineralogy, to describe the mineral emerald in 1806. In addition, we analyzed a rough emerald (1.51 carats, property of the Mel Fisher Maritime Heritage Society in Key West, Florida, USA) that is one of the 2300 stones recovered from the wreck of the *Nuestra Señora de Atocha* Spanish galleon, which sank off the coast of Florida in 1622 A.D. (*5*).

Ion microprobe oxygen isotopic analysis (*6*) shows that these emeralds have variable $\delta^{18}O$ values ranging from 7.5 per mil (‰) to 24.7‰. This range covers nearly all of the range known to exist in emerald deposits worldwide, that is, from 6.2 to 24.8‰ (*4*). It reflects variations in the isotopic composition of the hydrothermal fluids from which emeralds crystallized, the $\delta^{18}O$ value of the fluid being controlled by (i) the composition of the rocks through which the fluids were channeled (*7*), (ii) the intensity of the fluid-rock interactions, and (iii) the temperature of the fluid. Because the $\delta^{18}O$ values in each deposit typically span less than 1‰ (*8*), they are a good fingerprint of the origin of emeralds (Fig. 1). These can be combined with the gemological properties commonly used to characterize emeralds (*9*) in order to determine the origin of emeralds.

Egyptian pharaohs are supposed to have initiated the trade of emeralds by the exploitation of the Cleopatra mines (~1500 B.C.) (*2*). They traded emeralds to Asia, exchanging them for lapis lazuli from Afghanistan. Later, Habachtal emeralds in Austria, known by the Celts, were exploited by the Romans (*1*). Thus, on historical grounds, mines located in Egypt and Austria were the only sources of emerald in the world until 1545 A.D., when the Spaniards exploited the Colombian Chivor mines (*10*). This view is confirmed by the $\delta^{18}O$ value measured for the famous Saint

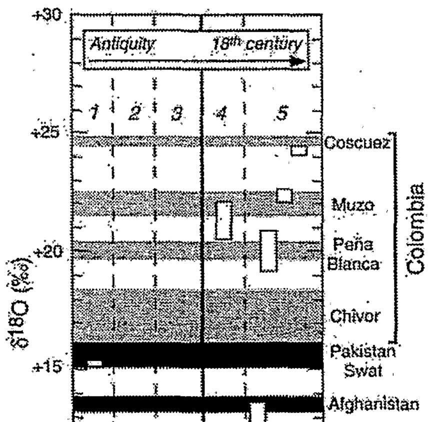

Fig. 1. The $\delta^{18}O$ values of the nine emeralds we analyzed (white boxes). This diagram shows the mining areas (black and gray fields) that are thought to have been exploited historically (*4*). The samples are ordered chronologically. All the samples have $\delta^{18}O$ values that are characteristic of a specific origin. 1: Gallo-Roman earring. 2: Holy Crown of France. 3: Hauy's emeralds. 4: Spanish galleon wreck. 5: old mine emeralds.

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Louis emerald of the crown of France, whose historical record goes back to 1226 A.D. (2). Its $\delta^{18}O$ value of 7.50 ± 0.5‰ (three analyses) is compatible with only three known emerald deposits, located in Austria ($\delta^{18}O$ = 7.1 ± 0.1‰), Zimbabwe ($\delta^{18}O$ = 7.5 ± 0.5‰), and Brazil ($\delta^{18}O$ = 6.8 ± 0.4‰). Because Brazil was discovered in the 16th century by the Portuguese and the Sandawana emerald deposit in Zimbabwe was discovered in 1956 (*11*), the $\delta^{18}O$ value of the Saint Louis emerald demonstrates its origin from the Habachtal mines in Austria. This is also in accordance with the observation that microscopic features characteristic of Sandawana emeralds—amphibole inclusions (actinolite, tremolite, and cummingtonite) and decrepitated fluid inclusions—are not observed in the Saint Louis emerald. In addition, mica crystals and aqueous-carbonic fluid inclusions comparable to those described for the Habachtal emeralds (*12, 13*) have been identified in the Saint Louis emerald. The two emeralds described by Abbé Hauy in 1806 have $\delta^{18}O$ values compatible with an origin from the Habachtal mines for sample H-3224 ($\delta^{18}O$ = 7.6, one analysis) and from Egypt for sample H-3255 ($\delta^{18}O$ = 10.5, one analysis).

The $\delta^{18}O$ value of the emerald from the Gallo-Roman earring discovered in Miribel shows that emerald sources other than Egypt and Austria were exploited in the world during antiquity. This emerald has a $\delta^{18}O$ value of 15.2 ± 0.3‰ (two analyses). The only known occurrence of emeralds with such a $\delta^{18}O$ value is the Swat-Mingora district in Pakistan, which contains emerald with values of 15.1 to 16.2‰ (Fig. 1). Thus, emeralds were mined or picked up from the Peshawar and Swat valleys. This result is consistent with the independent development of wealthy kingdoms in years B.C., such as Gandhara (grouping the Kabul, Peshawar, and Swat valleys) in what is now Pakistan and Afghanistan (*14*). During this period, long-distance trade routes were developing, and part of the Silk Route ran from the northern areas of Pakistan through the Peshawar, Swat, and Kabul valleys (Fig. 2). Because of their location along the Swat river, which is the natural geographic way of communication between Pakistan and Afghanistan, the emerald deposits of Swat-Mingora could have been discovered and exploited temporarily.

The existence of emeralds of exceptional gem quality in Colombia completely modified world trade of emeralds. The first Colombian emeralds were known in Europe before 1520 A.D. (*15, 16*). Soon after, the most important deposits were exploited by the Spaniards, in 1545 A.D. for the Chivor mines and 1594 A.D. for the Muzo mines. The rapid development of the trade of Colombian emeralds is demonstrated by the $\delta^{18}O$ value of the emerald recovered from the wreck of the *Nuestra Señora de Atocha* Spanish galleon, which sank off the coast of Florida in 1622 A.D. With a $\delta^{18}O$ value of 21.0 ± 0.8‰ (14 analyses), the provenance of this stone is clearly from the Muzo district in the western emerald zone of Colombia; more precisely, from the Tequendama mine (Fig. 1). This provenance cannot be located more precisely because emeralds were not registered in the manifest of the galleon, but the Colombian origin is consistent with the observation of fluid inclusions bearing three phases (*17, 18*) in several of the stones recovered from the wreck.

The $\delta^{18}O$ values demonstrate that emeralds mined in Colombia were traded throughout Europe and the Middle East and into India. The best examples of such stones are the old mine emeralds, whose origins were previously unknown (*1, 3*). Three of four such old mine emeralds coming from the treasure of the Nizam of Hyderabab (India) have $\delta^{18}O$ values demonstrating a Colombian origin (Fig. 1). These three emeralds come from three different mines, all located in the western emerald zone of Colombia: the Peña Blanca mine (*19*) for emerald OM441 (4.41 carats; $\delta^{18}O$ = 20.0 ± 0.8‰, eight analyses), the Coscuez mine for emerald OM618 (4.92 carats; $\delta^{18}O$ = 24.3, one analysis), and the Tequendama mine for emerald

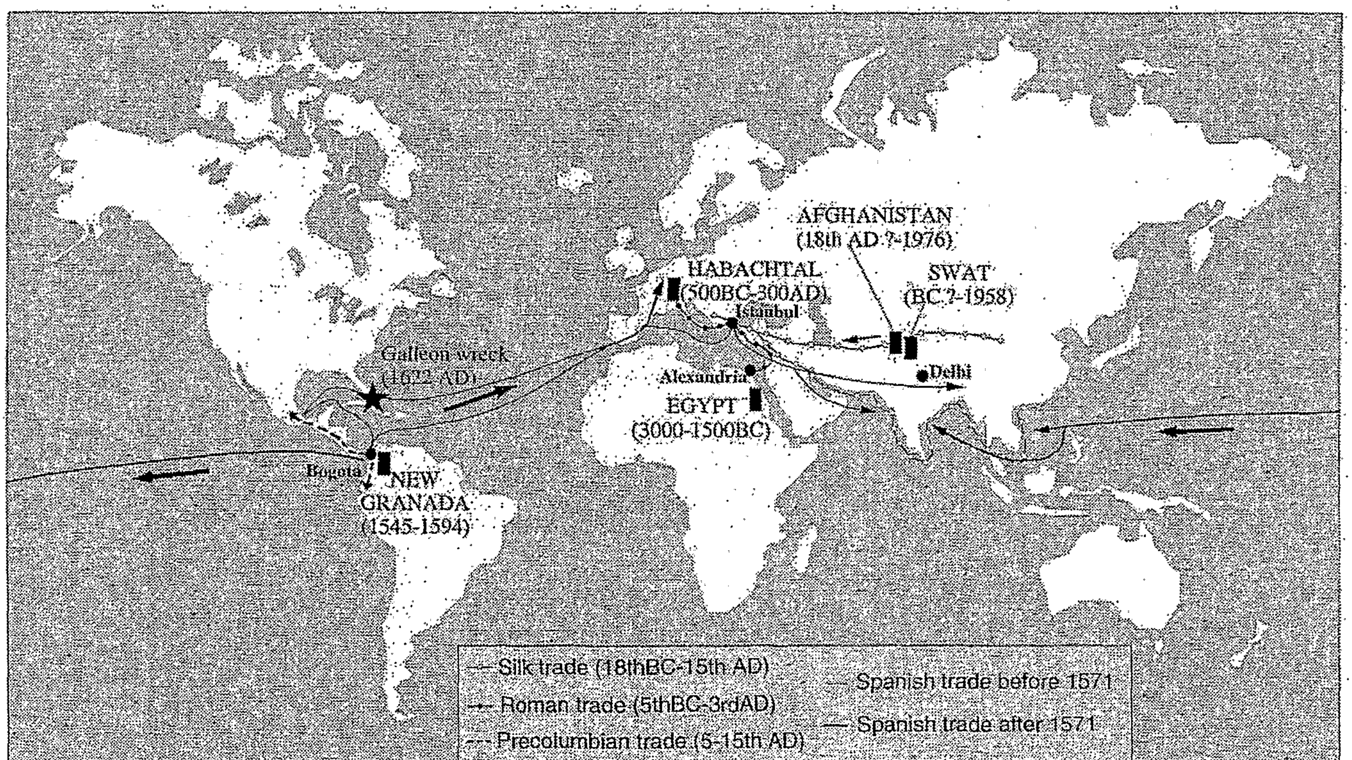

Fig. 2. Emerald trade routes. The five major routes claimed on historical grounds are indicated. The emerald deposits exploited historically are represented by black boxes and their supposed dates of exploitation are indicated in parentheses. The present $\delta^{18}O$ values of emerald demonstrate that the Silk Route was used to trade emeralds from Egypt, Pakistan, and Habachtal between Asia and Europe, and that since the beginning of the 16th century, the Spanish established the trade of Colombian emeralds to Asia, first across the Atlantic and then across the Pacific Ocean.

OM1361 (13.61 carats; $\delta^{18}O$ = 22.3, one analysis). This result contradicts the proposed origin of old mine emeralds from lost mines located in southeast Asia but validates gemological observations by Ward (*1*). The fourth old mine emerald analyzed (OM 451, 4.51 carats) has a value of 13.0 ± 0.6‰ (two analyses), which is suggestive of an origin in Afghanistan. Mines located in the Pansher valley in Afghanistan contain emeralds having $\delta^{18}O$ values ranging from 13.2 and 13.9‰ (*4*). These Afghan mines were mapped by the Soviets in 1976, but the $\delta^{18}O$ value of old mine emerald OM451 shows that these mines were already exploited at least as early as the 18th century.

The $\delta^{18}O$ values of old mine emeralds thus indicate that in the 17th and 18th centuries A.D., famous treasures found today in India, in the Topkapi Sarayi Palace and in the Markazi Bank, were constitued not only from New World stones (probably constituting the dominant fraction) but also, as previously proposed, from old Asian emeralds.

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3. F. H. Forestier and D. H. Piat, in *L'émeraude*, G. Giard, G. Giuliani, A. Cheilletz, E. Fritch, E. Gonthier, Eds. (Association Française de Gemmologie Press, Paris, 1998), pp. 139–145. Indian traders use the terms old mine emeralds or Moghul emeralds to designate emeralds of exceptional color, carat weight, cut, and clarity. These stones were cut in the 17th and 18th centuries A.D., but some of them might originate from older treasures. These emeralds have an unknown origin, but they are classically advocated to come from old mines lost in the past. They are also called "Bactriane" emeralds by historians who think that they were picked up by Alexander the Great in 300 B.C. during his far eastern conquest via the Pansher Valley in Afghanistan.
4. G. Giuliani *et al.*, *Miner. Deposita* **33**, 513 (1998).
5. The *Nuestra Señora de Atocha* galleon sank on 4 September 1622 off the coast of Florida when ravaged by a hurricane [E. Lyon, *Natl.Geogr.***149**, 786 (1976)]. In 1985, divers found the *Atocha* galleon and recovered gold, silver, and 2300 rough emeralds [E. Lyon, *Natl. Geogr.***161**, 228 (1982)].
6. The oxygen isotopic ratios ($^{18}O/^{16}O$) of the emeralds were determined with the CRPG-CNRS Cameca 1270 ion microprobe, using a Cs^+ primary beam and electron bombardment and analyzing in monocollection mode the ^{16}O and ^{18}O secondary ions at a mass resolution of ≈4500. Cut emeralds were oriented so that flat surfaces could be sputtered. The instrumental mass fractionation was calibrated on a set of emerald standards of different compositions and different crystallographic orientations previously measured in bulk by conventional mass spectrometry (*4*). The $^{18}O/^{16}O$ ratios were determined with a precision of ≈±0.6‰ (1σ) and are reported here with $\delta^{18}O$ notation, in per mil variations relative to the international standard mean ocean water standard, whose $^{18}O/^{16}O$ ratio is 2.0052 × 10^{-2}. The craters produced on the emeralds were ≈10 to 20 μm in diameter and of a few angstroms depth (≈2 × 10^{-11} g of an emerald were sputtered for one analysis). These spots are invisible to the naked eye, so this method can be considered nearly nondestructive and can be applied to gems of high value.
7. Emerald is the mineral beryl, $Be_3Al_2Si_6O_{18}$, in which a minor amount of Cr(V) is present. Two main types of emerald deposits are recognized worldwide (*4*): Type I, which corresponds to most of the deposits, involves the intrusion of granitic pegmatites within Cr(V)-bearing mafic-ultramafics. Type II emerald forms in thrusts, faults, and shear zones in Cr(V)-bearing rocks.
8. Emeralds can be classified in three groups according to their $\delta^{18}O$ values (*4*). The first group, with 6.2‰ < $\delta^{18}O$ < 7.9‰, includes emeralds from Brazil (Quadrilatero Ferrifero and Anagé districts), Austria (Habachtal, $\delta^{18}O$ = 7.1 ± 0.1‰), Australia (Poona), and Zimbabwe (Sandawana). The second group, with 8.0‰ < $\delta^{18}O$ < 12‰, includes most of the deposits in the world; that is, those of Zambia, Tanzania, Russia, Madagascar, Egypt ($\delta^{18}O$ = 10.3 ± 0.1‰), Pakistan (Kaltharo), and Brazil (Carnaíba and Socotó). The third group, with $\delta^{18}O$ > 12‰, includes the emerald deposits of Brazil (Santa Terezinha de Goiás), Afghanistan, Pakistan (the Swat-Mingora district), and Colombia (eastern zone, $\delta^{18}O$ = 16.8 ± 0.1‰; western zone, $\delta^{18}O$ = 21.2 ± 0.5‰).
9. The mineralogical and gemological data that are normally used to determine the origin of natural emeralds are the optical features (refractive indices and birefringence), density, adsorption spectra (ultraviolet and near-infrared), internal characteristics (growth phenomena and solid and fluid inclusions), and the chemical composition. However, the diagnostic value of these data is often restricted, because there may be an overlap for emeralds originating from different localities. On the other hand, the combination of mineralogical and gemological properties can be used, in many cases, to accurately identify emeralds from specific localities. Sometimes, even certain isolated data are highly characteristic. For example, emeralds from the Brazilian deposits of Salininha and Santa Terezinha, as well those from central Nigeria, can be identified by their spectroscopic data.
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15. The first Colombian emeralds in Europe were given to Hernán Cortés by the Aztec emperor Moctezuma II. These gifts were given to Charles Quint and were described by Albrecht Dürer in 1520. Some of these great samples, which were traded through Mesoamerica from the 10th century onward, are now curated at Vienna and Dresden (*16*).
16. P. Bariand and J.-P. Poirot, in *Larousse des pierres précieuses* (Librairie Larousse, Paris, 1985), pp. 133–142.
17. Primary fluid inclusions trapped in Colombian emeralds are typically brines. At room temperature, the degree of filling of the cavities is fairly constant. The inclusions typically contain a cubic crystal of halite (12 to 15 volume %), a brine (75 volume %), a vapor bubble (10 volume %), and sometimes a liquid carbonic phase (CO_2 liquid up to 3 volume %), which is easily visible in flat and large inclusions. These halite-bearing fluid inclusions are commonly used as the main criteria for diagnosis of Colombian emeralds, but they cannot be used to determine the origin more precisely to find the mine locality.
18. R. E. Kane *et al.*, *Gems Gemol.* **25**, 196 (1989).
19. Oxygen isotope analyses made with the classical fluorination technique (*4*) on the old mine emerald OM 441 gave a $\delta^{18}O$ value of 20.5 ± 0.3‰ (three analyses), which overlaps the value range defined by ion microprobe [$\delta^{18}O$ = 20.0 ± 0.8‰ (eight analyses)].

20. We thank the Mel Fisher Maritime Heritage Society in Key West, Florida, for providing a rough crystal from the *Nuestra Señora de Atocha* galleon. This is contribution CRPG-CNRS no. 1444.

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Quantum-Critical Conductivity Scaling for a Metal-Insulator Transition

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Temperature (*T*)- and frequency (ω)-dependent conductivity measurements are reported here in amorphous niobium-silicon alloys with compositions (*x*) near the zero-temperature metal-insulator transition. There is a one-to-one correspondence between the frequency- and temperature-dependent conductivity on both sides of the critical concentration, thus establishing the quantum-critical nature of the transition. The analysis of the conductivity leads to a universal scaling function and establishes the critical exponents. This scaling can be described by an *x*-, *T*-, and ω-dependent characteristic length, the form of which is derived by experiment.

A quantum phase transition (QPT) is a zero-temperature, generically continuous transition tuned by a parameter in the Hamiltonian at which quantum fluctuations of diverging size and duration (and vanishing energy) take the system between two distinct ground states. Examples of QPT include the integer and fractional Quantum-Hall transitions, magnetic transitions of cuprates or heavy-Fermion alloys, and metal-insulator and superconductor-insulator transitions in disordered alloys (*1*).

These transitions are intrinsically complicated because of strong interactions between electrons and the frequent presence of static disorder (*2*). However, two features specific to QPTs make them amenable to experimental and theoretical study: (i) the diverging length and time scales of the fluctuations that drive the transitions favor the use of scaling relations (*3*) in describing experimental results, and (ii) the dominance of quantum fluctuations near the

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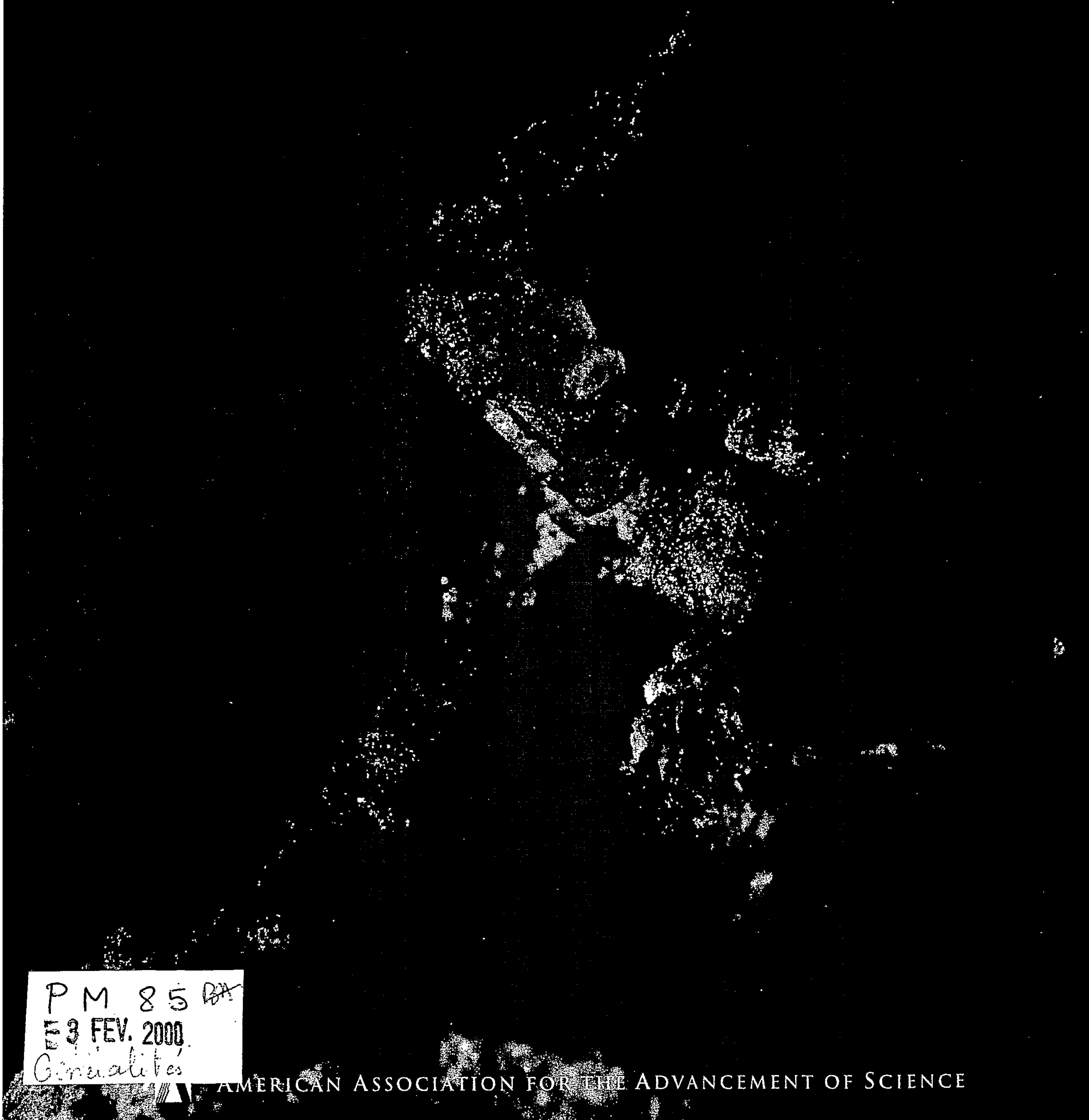

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