PERSPECTIVES: PLANETARY SCIENCE

Salty Old Rocks

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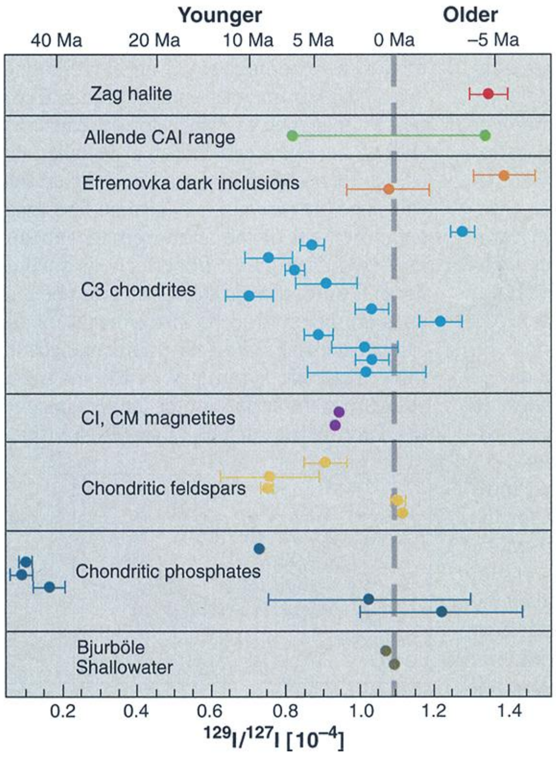
Everybody is familiar with common salt, sodium chloride (NaCl), or halite as it is called by mineralogists. On Earth, most salt is contained in the oceans, and its occurrence is generally closely connected with the presence of water. This is why the observation of salt (and other minerals associated with water) in martian meteorites (*1*) has been interpreted as evidence supporting the former presence of water on Mars. But ordinary chondrites—the most common meteorites, dry rocks that show evidence of having been heated up to several hundred degrees Celsius—might not seem to be the most logical place to search for halite. According to two recent reports (*2*, *3*), however, crystals of halite have been found in just this type of meteoritic rock. On page 1819 of this issue, Whitby *et al.* (*4*) show unequivocally that the halite grains in one of these meteorites are of extraterrestrial origin. They also determine their age, as do Garrison and Bogard for halite in the other meteorite (*5*). It comes as a surprise that the results put these grains of salt among the oldest materials found in the solar system.

Evidence for the former presence of water in primitive meteorites—those only little affected by thermal metamorphic processes on their parent body—is abundant (*6*). But the chondrites in which halite was recently found are not very primitive: One of them, the Zag meteorite, consists of fragments spanning the range from primitive to highly metamorphosed, and the other, Monahans, is highly metamorphosed throughout.

According to previous age dating of aqueous alteration products, aqueous alteration of primitive meteorites must have happened early in the history of the solar system, less than 100 million years after formation of the solar system 4.57 billion years ago (*6*), but otherwise the timing has been poorly constrained. The advantageous elemental composition of halite has now allowed fairly reliable ages to be determined (*4*, *5*). The chemical closeness of potassium to sodium and of iodine to chlorine assures the presence of the radioisotope ^{40}K and its decay product ^{40}Ar, as well as the decay product of ^{129}I— ^{129}Xe— in the halite grains. This, together with the extreme sensitivity of the state-of-the-art RELAX mass spectrometer at Manchester, allows application of argon-argon and iodine-xenon dating to samples of only some tens of micrograms (*4*).

The results from the I-Xe dating by Whitby *et al.* (*4*) are particularly astonishing. The isotope ^{129}I (with a half-life of 15.7 million years) is an extinct radioisotope that was present in the early solar system with an abundance ratio relative to stable ^{127}I of about 1×10^{-4}, which has decayed away into ^{129}Xe. In I-Xe dating, irradiation of a sample with reactor neutrons converts part of ^{127}I into ^{128}I, of which 93% decays into stable ^{128}Xe. The ratio ^{129}I/^{127}I at the time the mineral formed is then determined from a measurement of ^{129}Xe/^{128}Xe. Whitby *et al.* (*4*) find ^{129}I/^{127}I ratios ranging from 1.03×10^{-4} to 1.83×10^{-4}, with a weighted mean of $(1.35 \pm 0.05) \times 10^{-4}$. Chronologically, this puts Zag halite formation at 4.8 ± 0.8 million years before the formation of the Bjurböle chondrite, a meteorite often used as a reference (see the figure). Zag halite is thus among the oldest samples dated by I-Xe, even more so given a recent reexamination, which indicates that several of the heretofore oldest I-Xe ages need be revised downward (*7*) (see the figure).



Ancient meteorites. Lower abscissa: ^{129}I/^{127}I at time of formation. Upper abscissa: I-Xe age relative to the Shallowater standard [absolute age (4566 ± 2) million years] (*9*). Phosphate and feldspar data from ordinary chondrites are taken from (*9*); Efremovka dark inclusions ages and Allende CAI age range are from (*10*). Several previously reported I-Xe ages for C3 chondrites and for magnetites of the Orgueil (CI) and Murchison (CM) carbonaceous chondrites (*11*) have been adjusted, with the use of the revised age for Murchison magnetite (*7*). Note that in their discussion, Whitby *et al.* (*4*) refer to the uncorrected ages.

Overall, the results are well explained in a scenario in which the halite grains formed very soon after the accretion of their parent body by evaporation of a brine, followed about 300 million years later (around 4.22 billion years ago) by a large impact that brought together the various constituents of the Zag meteorite, including the halites. It is clear that, if halite formation occurred inside the asteroid, it must postdate the formation of the first solids by the amount of time it took to accrete the parent asteroid and develop the right conditions for aqueous alteration. If the I-Xe age of the Zag halite is correct, this time must have been extremely short. As a consequence, one may need to keep an open mind regarding the question to what extent aqueous alteration could also have happened in the solar nebula, rather than solely on asteroidal parent bodies.

The discovery of halite in these two freshly fallen ordinary chondrites also suggests that its occurrence may be more widespread than previously assumed. It may simply have been overlooked in the past (*3*), perhaps in part because of the extreme sensitivity of halites to terrestrial weathering.

One important point is not addressed in the report by Whitby *et al.* (*4*), nor in the similar analyses of halite grains from Monahans (*5*). If the I-Xe age for the halite rivals that of the Ca-Al–rich inclusions (CAIs) in the famous Allende meteorite (see the figure), formed (4566 ± 2) million years ago and generally regarded as the oldest material formed within the solar system, then the presence of radionuclides with even shorter half-lives than that of ^{129}I may be expected. Given the chemical composition of halite, ^{36}Cl (with a half-life of 0.3 million years) would be the prime candidate. Calculations of the abundance of radionuclides in the early solar system predict ^{36}Cl/^{35}Cl ratios on the order of 10^{-6} at the time the CAIs were formed (*8*), which would have decayed to $\sim 10^{-8}$ within 2 million years. The Ar analyses in (*4*) and (*5*) do show high concentrations of the decay product ^{36}Ar

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in the halites, corresponding to $^{36}Cl/^{35}Cl \sim 10^{-8}$. But, unfortunately, there is another possible source for the ^{36}Ar, namely the capture of thermal neutrons by ^{35}Cl, which may have occurred during recent cosmic ray exposure in transit to Earth and/or during the time the halite spent on its parent body (*4*, *5*).

With the currently available data, there is no simple unambiguous way to decide between the source of ^{36}Ar, but the observed ratio of ^{36}Ar to ^{35}Cl of about 1×10^{-8} at least provides an upper limit for the ratio $^{36}Cl/^{35}Cl$ at the time of halite formation. More work along the lines pioneered by Whitby *et al.* (*4*) will be required to see how compatible the Ar and Xe data are with each other. The search for neutron effects in other elements may help to determine the origin of ^{36}Ar.

Some of the finer details of I-Xe dating are only now being understood (*7*, *9*). In the Zag halites, the system is disturbed (*4*), as shown by the variation in the $^{129}I/^{127}I$ ratios inferred from different extraction steps, which is larger than can be ascribed to analytical errors of the individual values. This variation may have been caused by shock from the impact that brought together the various meteoritic constituents 4.22 billion years ago. It is clear that halite formation must have occurred very early, but the absolute age and the lessons we think we have learned may have to be taken with a grain of salt.

References

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PERSPECTIVES: ANTIFERROMAGNETISM

Taking a Very Close Look at Magnetic Structures

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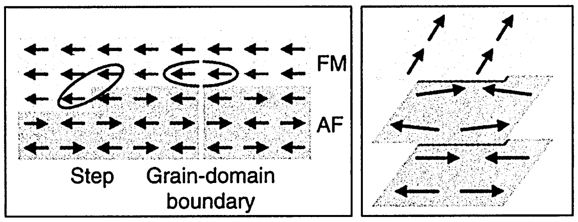
Magnetic materials are key components in today's information technology. Large amounts of data are stored in thin magnetic films on computer hard disks. Magnetic multilayer structures also serve as miniaturized and very sensitive magnetization sensors. Future integrated magnetic elements may even compete with traditional semiconductor technology, for example, as fast nonvolatile random access memory.

To meet the ever-increasing demands on storage density, processing speed, and device complexity, researchers must learn how to control their materials' structure, composition, and magnetic properties on a sub–100-nm scale. This will require advanced tools not only for the fabrication but also for the microscopic characterization of the magnetic structures. On page 1805 of this issue, Heinze *et al.* (*1*) use an innovative scanning probe method to image an antiferromagnetically ordered Mn monolayer with atomic spatial resolution. This is a considerable advance, considering that previous characterizations of antiferromagnetic domains could not go beyond micrometer resolution.

Antiferromagnetic layers are essential components in magneto-electronic devices, because they are insensitive to external magnetic fields. In an antiferromagnetic material, the direction of the magnetic moment alternates from lattice site to lattice site, with no overall macroscopic magnetization. Placed next to a ferromagnet, an antiferromagnet "pins" the ferromagnet's magnetization direction by magnetic exchange forces, causing a shift in the hysteresis loop that is called exchange bias. Modeling studies indicate that exchange bias is caused by a small ferromagnetic moment of the antiferromagnetic surface (see the figure). Imperfections such as domain walls, atomic steps, and grain boundaries are believed to be instrumental for the appearance and size of this moment, because they break the symmetry of the magnetic structure at the surface of the antiferromagnet (*2*). Pure metals such as Cr or Mn, transition metal alloys such as FeMn or IrMn, and transition metal oxides such as Fe_2O_3 (hematite) exhibit antiferromagnetism. Other oxide compounds, like the manganites known for the colossal magneto-resistance effect, can be antiferromagnets or ferromagnets depending on doping and temperature (*3*).



Competing models for the origin of exchange bias at the interface between an antiferromagnet (AF) and a ferromagnet (FM). (Left) Coupling by uncompensated moments at steps or grain-domain boundaries generates uncompensated magnetic moments (marked with ovals) on an ideal, completely compensated antiferromagnetic surface. A net coupling results from an imbalance of parallel (red) and antiparallel (green) oriented moments. **(Right)** Spin-flop models assume a 90° angle between the magnetization of the FM and the AF. The moments at the surface of the AF are canted in the direction of the magnetization of the FM (if the coupling between FM and AF is ferromagnetic), leading to the formation of a parallel domain wall. In both models, the ferromagnetic moment at the surface of the AF pins the magnetization direction of the FM, thus causing exchange bias.

The investigation of the magnetic structure of antiferromagnets is difficult because of the lack of a macroscopic magnetization. This has hampered attempts to determine the microscopic origins of exchange bias. Large magnetic domains in single-crystal antiferromagnets were imaged by optical methods (*4*) as early as the 1950s. More recently, it has become possible to resolve micrometer-sized antiferromagnetic domains with x-ray spectromicroscopy (*5*), but imaging of domains in technologically important materials with typical grain sizes around 10 nm has remained out of reach (*6*). Heinze *et al.* have now gone a step further, imaging the antiferromagnetic surface structure of a magnetically ordered Mn monolayer with atomic spatial resolution by applying spin-polarized scanning tunneling microscopy (SP-STM), a method pioneered by the authors in the early 1990s (*7*). More than 10 years ago, Blügel *et al.* predicted that such a Mn monolayer would form an ideal two-dimensional antiferromagnet (*8*). But this prediction remained unconfirmed until now, because the magnetic configuration could not be determined by conventional, bulk sensitive techniques like neutron scattering owing to the minute amount of magnetic material contained in a single monolayer.

Unlike conventional magnetic force microscopy, which measures the magnetic dipole force between magnetic sample and

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