Reports

The Widespread Distribution of a Novel Silica Polymorph in Microcrystalline Quartz Varieties

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An x-ray examination of more than 150 specimens of fine-grained quartz varieties from around the world has revealed that more than 10% and as much as 80% of the silica in many samples is actually moganite, a little-known silica polymorph. Rietveld refinements of 50 powder x-ray diffraction patterns produced by fibrous quartz (agate, chalcedony) and nonfibrous quartz (chert, flint) indicate that the concentrations of moganite within each subgroup are widely distributed. The large amount of moganite (>30%) found in cherts from arid, alkaline environments may resurrect length-slow silica as an indicator of evaporitic regimes, and the absence of moganite in weathered and hydrothermally altered silica samples may be a useful measure of fluid-rock interaction.

BECAUSE IT COMPRISES 12% OF THE earth's crust by volume, quartz (SiO_2) demands the attention of earth scientists by virtue of its sheer abundance, and it probably has been more exhaustively investigated than any other mineral. Moreover, the piezoelectric nature and high quality factor of quartz account for its immense popularity as an electronic oscillator. Quartz in microcrystalline form is common to a wide variety of geological settings, and it long has been valued in the form of such semiprecious gems as onyx, jasper, and agate. In light of the intensive scrutiny quartz has received, many scientists may find it surprising to learn that most microcrystalline quartz varieties consist not only of quartz but also of a distinct silica polymorph called moganite.

We examined more than 150 samples of fine-grained silica from the mineral collection of the U.S. National Museum of Natural History using automated powder x-ray diffraction techniques. Virtually every pattern produced by microcrystalline quartz samples contained some peaks that could be attributed only to moganite, a phase identified and described in the mid-1970s by Flörke *et al.* (*1*) from the ignimbrites of the Mogan formation on Gran Canaria. Later work revealed trace quantities of moganite in some samples of flint and chalcedony (*2*), and the moganite structure was refined by means of powder neutron diffraction (*3*). Nevertheless, the occurrence of this mineral is not well known, and there has been skepticism as to whether it is even a distinct phase. As evidence, moganite has not yet been approved by the Commission on New Minerals and Mineral Names (*4*).

Historically, microcrystalline quartz varieties have been classified into a veritable menagerie of subspecies (*5*), and the distinctions separating these groups are highly arbitrary. We refined 50 of the 150 diffraction patterns produced by fine-grained quartz samples using the Rietveld technique (*6*) to determine whether fine-grained quartz varieties are distinguishable on the basis of moganite content. This approach allowed us not only to corroborate the presence of the additional silica phase but to quantify the amount of moganite contained within the various classes of fine-grained quartz (7).

The specimens were separated into fibrous and nonfibrous varieties, as ascertained with the petrographic microscope. Fibrous varieties were further divided into agate, which occurs in concentrically banded nodules, and chalcedony, which typically displays no banding. Nonfibrous varieties that displayed the gray color and unctuous texture associated with flint were classified accordingly, and all other samples were labeled generically as chert.

With the exception of the Arkansas novaculite, Rietveld refinement of these microcrystalline silica varieties revealed that at least some moganite was present in every unaltered specimen (Fig. 1). In light of the natural abundance of fine-grained quartz, these results suggest that moganite is a fairly common mineral of the earth's crust. The data also suggest that the amount of moganite contained within microcrystalline quartz cannot be used as a means of classification. Both agate and chalcedony exhibited a range of moganite contents from somewhat more than 20% (by weight) to less than 5%, although within our limited sampling the chalcedonies as a group tended to contain more moganite than the agates. The samples labeled as chert displayed an even wider variation, from more than 75% to less than 5% moganite. With the exception of the specimen from the Deep Sea Drilling Project (DSDP), the flint samples uniformly contained between 13 and 17% moganite. Although they occur in different countries, these flint samples are from the same geological unit; they occur as nodules from the Upper Cretaceous chalk beds that cover much of western Europe.

This range of distribution would seem to indicate that moganite can form under ostensibly different environmental conditions. Specimens containing more than 20% moganite include an agate from Denmark, silicified coral from Hillsborough Bay, Florida, and chert from Lake Magadi, Kenya. All of these samples presumably formed at relatively low temperatures and pressures, but their petrogeneses clearly differ. The agate precipitated from silica-rich hydrothermal fluids that percolated through gas cavities of a volcanic host rock (*8, 9*). The fossilized coral apparently formed by a replacement of biogenic carbonate during interaction with ground waters that were undersaturated with respect to silica (*10*). The cherts of Lake Magadi were produced when ground waters leached Na from precursor magadiite [$NaSi_7O_{13}(OH)_3 \cdot 3H_2O$] (*11*).

The field of thermodynamic stability for moganite thus remains uncertain. The most moganite-enriched samples originated from Gran Canaria (65 to 85% moganite) and Lake Magadi (30 to 45% moganite). Both these localities are extremely arid. The chert nodules in the ignimbrites of Gran Canaria are exposed in caliche-like zones containing pockets of gypsum [$CaSO_4 \cdot 2H_2O$] and halite [NaCl]. Likewise, Lake Magadi is an evaporitic basin with extensive deposits of alkaline carbonates and hydroxides. Consequently, the field associations suggest that high activities of alkalis, sulfates, or both may play a role in the crystallization of moganite.

The affiliation of moganite with evaporitic regimes may account for the common association of length-slow chalcedony, or lutecite, with vanished evaporite deposits (*12*). Moganite is fibrous and virtually indistinguishable from chalcedony with the petrographic microscope except that optically moganite is length-slow. We suggest that

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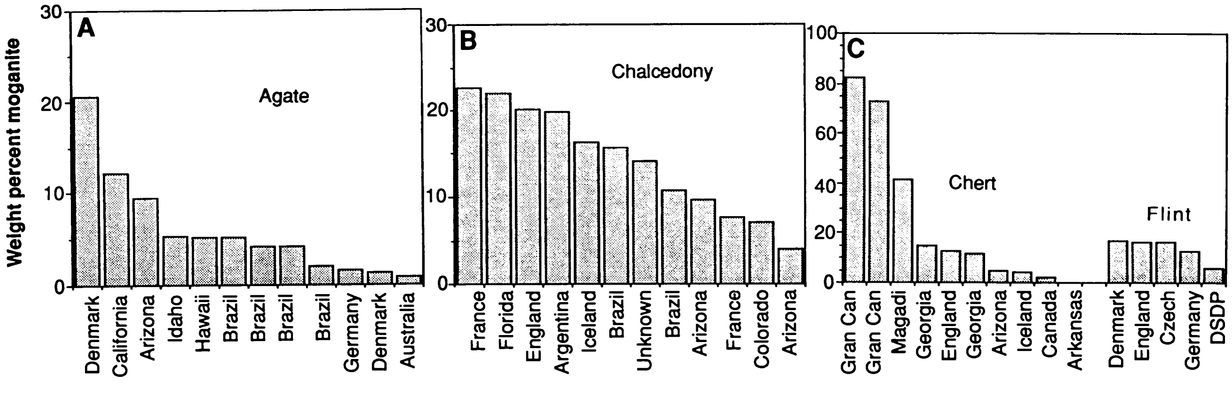

Fig. 1. Plots of weight percent moganite in microcrystalline silica samples from the Mineral Collection in the U.S. National Museum of Natural History, as determined by Rietveld refinement of powder x-ray diffraction patterns. (**A** and **B**) Fibrous quartz varieties; (**C**) nonfibrous quartz varieties. For each specimen the complementary phase was pure quartz.

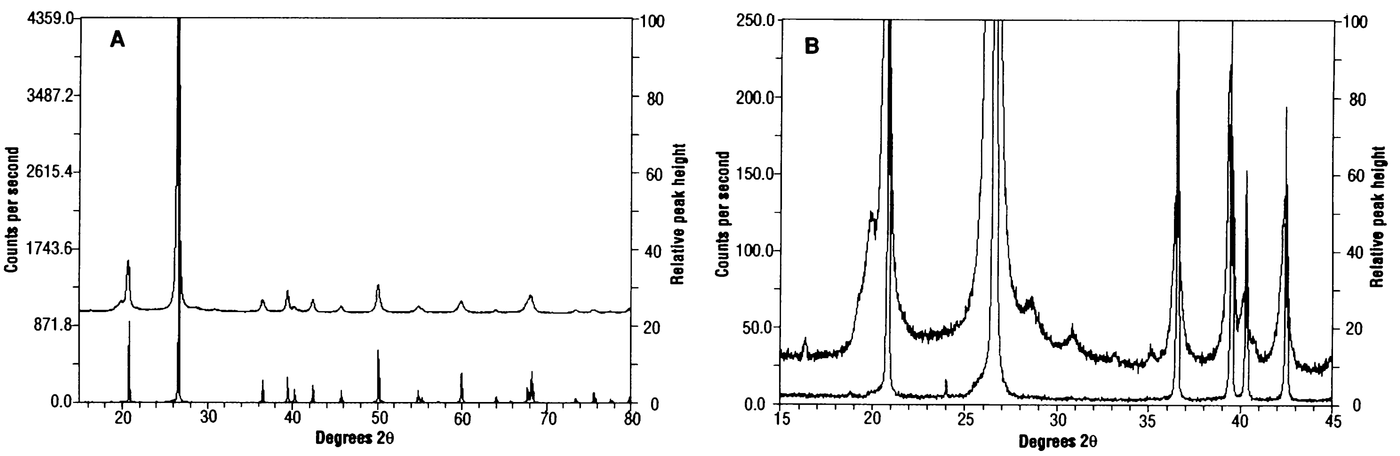

Fig. 2. (**A**) X-ray powder diffraction patterns of pure macroscopic quartz from Hot Springs, Arkansas (bottom), and chalcedony from fossilized coral, Hillsborough Bay, Florida, with 22% moganite (top). Peak broadening can be seen in the chalcedony pattern, but at this scale the patterns appear quite similar. (**B**) Enlargement of the above diffraction pattern more clearly reveals extra peaks associated with moganite intergrowths.

much of the so-called lutecite associated with evaporitic minerals actually is moganite, although our experiments demonstrate that some length-slow silica does refine as quartz. Indeed, the term lutecite was fabricated as a new mineral name by Michel-Lévy and Munier-Chalmas (*13*) to describe a length-slow silica phase intimately intergrown with length-fast chalcedony from the evaporitic gypsum beds of the Paris Basin. The Mineral Collection of the National Museum houses material donated in 1895 by the Paris Museum and labeled "lutecite" from the type locality, Clamart, France. Rietveld refinement of this specimen revealed it to contain 23% moganite and 77% quartz.

It would seem, then, that moganite actually is a rediscovery of lutecite, a mineral name abandoned by mineralogists but retained for casual usage among petrologists to describe length-slow chalcedony. Mineralogists eschewed the term after powder x-ray diffraction experiments of fibrous silica in the early part of this century demonstrated only the presence of quartz (*14*). Indeed, a comparison of the x-ray powder diffraction pattern produced by moganite-rich chalcedony with that of pure quartz (Fig. 2) reveals the source of the confusion: Many of the major peaks of quartz overlie those of moganite, and identification of moganite requires extreme magnification of the pattern.

The similarity of the diffraction patterns produced by moganite and quartz can be attributed to their structural kinship. As was first determined by Miehe *et al.* (*3*), the moganite structure can be envisioned as slices of left- and right-handed quartz alternating at the unit-cell scale along the (101) planes. The proposed space group is $I2/a$ ($=C2/c$), and selected-area electron diffraction patterns produced by moganite (*2*) exhibit the doubled periodicity along [101]* required by the model.

Our sampling of specimens from Gran Canaria indicates that moganite occurs as two phenotypes. The first, described by Flörke *et al.* (*1*), is massive, nodular or seam-filling, and macroscopically indistinguishable from chert. We observed a second variety as a white powder surrounding selected nodules in a coating approximately 0.5 cm thick. Rietveld refinement of these unconsolidated powders revealed that they are the purest samples analyzed, containing more than 80% moganite. In transmission electron microscope images of this material (Fig. 3), individual grains appear to be composed of laths that measure 100 Å thick and 0.5 μm long. In some instances these laths overlie one another at an angle of 49° in projection; this pattern creates an unusual chevron-like texture (*15*).

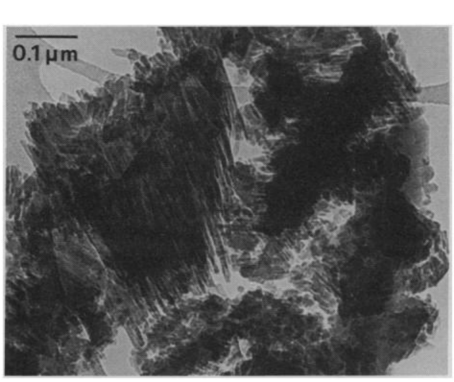

Fig. 3. Transmission electron microscope image of purest moganite sample recovered from Gran Canaria (83% moganite) indicates that particles are composed of individual laths approximately 100 Å thick.

Although nearly all of the unaltered specimens that we examined contained some moganite, six samples known to have been exposed either to surface weathering or to hydrothermal fluids revealed virtually no moganite upon Rietveld refinement. Chalcedony stalactites, jaspers from Precambrian banded iron formations, and the weathered white rinds of agate nodules refined as pure quartz. This observation suggests that either moganite readily recrystallizes to quartz in the presence of water or that moganite has a higher solubility in water than does quartz. Boiling 10 g of powdered chert containing 73% moganite in a flask of water for 2 months at surface pressure induced no measurable change in the relative concentrations of the two phases. However, numerous studies (*16*) have demonstrated that chalcedony is significantly more soluble than macrocrystalline quartz in water. In light of the ubiquitous presence of moganite in chalcedony, we suggest that the higher solubility of chalcedony may be attributed to its moganite component. Our results indicate that moganite is so prevalent in unaltered specimens that its absence in microcrystalline quartz varieties may be useful as an indicator of fluid-rock interactions.

REFERENCES AND NOTES

1. O. W. Flörke, J. B. Jones, H.-U. Schminke, *Z. Kristallogr.* **143**, 156 (1976); O. W. Flörke and U. Flörke, *Neues Jahrb. Mineral. Abh.* **149**, 325 (1984).
2. H. Graetsch, O. W. Flörke, G. Miehe, *Phys. Chem. Minerals* **14**, 249 (1987).
3. G. Miehe, H. Graetsch, O. W. Flörke, H. Fueß, *Z. Kristallogr.* **182**, 183 (1988).
4. Although moganite is not an approved mineral name, the term is used extensively in the literature above (*1–3*), and we have adopted it here.
5. For details see C. Frondel, *The System of Mineralogy*, vol. III (Wiley, New York, 1962).
6. Samples were ground in porcelain mortars under acetone and smeared onto low-background quartz plates, sieved onto glass fiber-filters, or pressed into pack mounts. The data were obtained on a Scintag computer-automated powder x-ray diffractometer with CuKα radiation and an intrinsic-Ge solid-state detector. Counting times ranged from 2 to 10 s per 0.03° step for the 2θ range 3° to 80°. Rietveld refinement was carried out using the computer program DBW3.2 by D. B. Wiles and R. A. Young [*J. Appl. Cryst.* **14**, 149 (1981)] as modified by S. A. Howard. Only data from $28° < 2\theta < 80°$ were used for refinement. Refined parameters included scale factor, background, sample displacement, peak width, peak shape, and unit cell dimensions. Starting unit cell parameters for quartz were taken from A. F. Wright and M. S. Lehmann [*J. Sol. State Chem.* **36**, 371 (1981)], and starting parameters for moganite were taken from Miehe *et al.* (*3*). Final ratios for R_{wp} to expected R_{wp} (where R_{wp} is the agreement index of the refinement) ranged between 1.1 and 2.3, and most values were less than 1.5.
7. Quantitative analysis with Rietveld refinement is outlined by R. L. Snyder and D. L. Bish in *Modern Powder Diffraction*, D. L. Bish and J. E. Post, Eds. (Mineralogical Society of America, Washington, DC, 1989), pp. 101–144.
8. I. Sunagawa and E. Ohta, *Sci. Rep. Tohoku Univ.* **13**, 131 (1976).
9. O. W. Flörke, B. Köhler-Herbertz, K. Langer, I. Tönges, *Contrib. Mineral. Petrol.* **80**, 324 (1982).
10. E. H. Lund, *Am. Mineral.* **45**, 1304 (1960).
11. H. P. Eugster, *Contrib. Mineral. Petrol.* **22**, 1 (1969).
12. See R. L. Folk and J. S. Pittman, *J. Sed. Petrol.* **41**, 1045 (1971). The presence of length-slow silica in abyssal Pacific chert [J. B. Keene, *Sedimentology* **30**, 449 (1983)] and carbonate turbidites [A. D. Jacka, *J. Sed. Petrol.* **44**, 421 (1974)] indicates that lutecite is not restricted to near-surface deposits. M. Kastner [*Eos* **61**, 399 (1980)] found that length-slow quartz could be crystallized in slightly alkaline solutions (pH = 7 to 9) enriched in Mg^{2+}, Na^{+}, and SO_4^{2-}. Nevertheless, length-slow chalcedony remains a marker for vanished evaporites. An extensive review of the associations of length-slow chalcedony with evaporites can be found in I. Hattori, *Siliceous Deposits of the Tethys and Pacific Regions*, J. R. Hein and J. Obradovic, Eds. (Springer-Verlag, New York, 1989), pp. 201–215.
13. A. Michel-Lévy and C. P. E. Munier-Chalmas, *Bull. Soc. Fr. Minéral.* **15**, 159 (1892).
14. E. W. Washburn and L. Navias, *Proc. Natl. Acad. Sci.* **8**, 1 (1922).
15. Specimens were ground under alcohol and deposited as crushed grains on holey-carbon support films. Transmission electron microscopy was performed on a JEOL 1200-CX operating at 120 keV.
16. C. R. Pelto, *Am. J. Sci.* **254**, 32 (1956); R. O. Fournier and J. J. Rowe, *Am. J. Sci.* **264**, 685 (1966); S. Arnorsson, E. Gunnlaugsson, H. Svavarsson, *Geochim. Cosmochim. Acta* **47**, 567 (1983).

17. We thank D. Ross for aid in specimen preparation. D. Hope kindly allowed us the use of his transmission electron microscope in the Division of Worms, National Museum of Natural History, and D. Veblen offered helpful discussions. J. R. Hein and P. Barton lent specimens used in this study.

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Shocked Quartz at the Triassic-Jurassic Boundary in Italy

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Quartz grains that appear to have been shock-metamorphosed occur within three closely spaced shale beds from the uppermost Triassic ("Rhaetian") Calcare a Rhaetavicula in the Northern Apennines of Italy. The upper shale coincides with the abrupt termination of the distinctive, uppermost Triassic *Rhaetavicula* fauna and is overlain by the Hettangian (Lower Jurassic) Calcare Massiccio; no extinctions appear to be associated with the two lower layers, which occur 1.2 and 2.4 meters below the boundary shale. Approximately 5 to 10% of the quartz grains within these layers exhibit one or more sets of planar deformational features whose orientations cluster around the rational crystallographic planes (basal, ω, and π) most commonly observed in shocked quartz. Textural and stratigraphic observations support an interpretation of at least three closely spaced impacts at the end of the Triassic.

THE TRIASSIC-JURASSIC (T-J) boundary represents one of the five most severe marine extinctions in Phanerozoic history (*1, 2*) and is a time of important terrestrial extinctions (*3–7*). Several groups of marine invertebrates experienced particularly heavy losses. Ammonoids, bivalves, gastropods, and corals suffered high familial extinctions, and conodonts disappeared completely (*8–11*). At the species level, the frequencies of molluscan extinction were exceedingly high; Hallam (*8*) estimated that 92% of northwest European bivalve species became extinct, and fewer than three lineages of ammonoids survived (*8, 12*). As with the other major mass extinctions in Earth history, the cause of the T-J extinctions has been uncertain (*3, 4, 8, 9*). Recent developments supporting one or more asteroid or comet impacts as the primary cause of the Cretaceous-Tertiary (K-T) mass extinctions (*13–16*) have led to speculation that extraterrestrial impacts had a role in other mass extinction events (*17*). In order to investigate the possible connection between the T-J extinctions and a possible impact event, it is necessary to locate the ejecta from the impact within a fossil-bearing stratigraphic sequence, a task made difficult by the apparent scarcity of complete T-J sections (*8*).

In this report, we provide evidence that suggests a contemporaneous relation between impact ejecta and extinctions from a boundary section in the Il Fiume gorge near the village of Corfino in Northern Tuscany. In this region, the T-J boundary is considered to occur at the stratigraphic contact between the uppermost Triassic ("Rhaetic" or upper Norian) Calcare a Rhaetavicula and the Lower Jurassic (Hettangian) Calcare Massiccio (*18, 19*).

At Corfino, Rhaetic limestones consist of two principal facies: about 80% of the section is skeletal packstone and wackestone; the remaining 20% is biomicrite and sparse biomicrite (Figs. 1 and 2A). Calcareous shale is interbedded with the limestone. The skeletal packstone-wackestone facies is abun-

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