

**ORIGIN AND DIAGENESIS OF CHERTS:  
AN ISOTOPIC PERSPECTIVE**

**L. Paul KNAUTH**

Department of Geology, Arizona State University  
TEMPE, Arizona 85287 (U.S.A.)

Cherts most commonly consist of microcrystalline quartz which has replaced precursor sedimentary materials. They occur in a variety of sedimentary associations of all ages and are thus attractive targets for isotopic studies. The origin of most chert types remains controversial, but isotopic investigations have allowed a greatly improved understanding of the timing and conditions under which silica diagenesis proceeds. Isotopic data on cherts also play a key role in the ongoing controversies regarding the isotopic history of ocean water and the climatic history of the earth.

At this stage, there have been a few broad surveys of the authigenic silica system, and several aspects of chert diagenesis have been examined in detail. However, the field is still largely unexplored due to the great diversity of chert types and the complexity of the silicification process. Considering the extraordinary range of isotopic variation that has been so far encountered, it seems likely that major discoveries and surprises are still ahead. This contribution presents an overview of the low temperature silica system and summarizes isotopic results for the major chert types.

## GEOLOGY OF CHERTS AND OTHER AUTHIGENIC SILICA

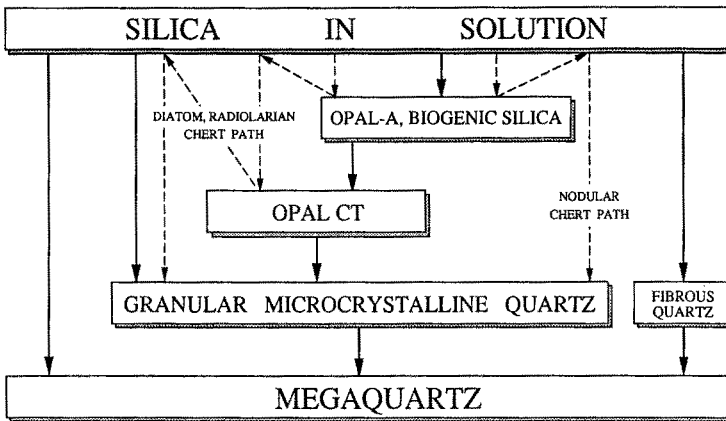
Authigenic silica occurs in sediments as 3 types of opal and 5 types of quartz (Table 1). The room-temperature solubility values are approximately independent of pH below 9. Any diagenetic fluid carrying more than 6 mg/g dissolved silica is potentially a silici-fying fluid. At values above about 80 mg/g, it is likely that one of the more amorphous phases (opal-CT, opal-A) will precipitate instead of quartz.

Table 1

<u>SILICA PHASE</u>	<u>CHARACTERISTICS</u>	<u>SOLUBILITY AT 25°C</u> (Approx. ppm)
<u>OPAL</u>		
Opal-A	Isotropic, amorphous silica. Diffuse x-ray peak at 4.1 Angstroms. Up to 12 wt.% H <sub>2</sub> O.	120
Opal-CT	V. low biref. Diffuse x-ray pattern containing weak peaks characteristic of $\alpha$ -cristobalite and $\alpha$ -tridymite. 0.5 to >1 Wt. % H <sub>2</sub> O	80
Opal-C	X-ray pattern containing well defined peaks of alpha cristobalite. V. rare in sediments. H <sub>2</sub> O content unknown.	?
<u>QUARTZ</u>		
Granular Micro- crystalline quartz	8-micron grain size, intergrown grains not ordered over the long range. Irreg. extinction. 0.2 - 1.2 wt.% H <sub>2</sub> O.	>6?
Megaquartz	Pin point extinction, regular grain boundaries. Each grain is a crystal of $\alpha$ -quartz. H <sub>2</sub> O as fluid inclusions	6
Fibrous quartz:	H <sub>2</sub> O content up to 1.0 wt.%, or more.	>6?
Length-fast	Bundles of fibrous quartz length fast over entire length of fiber.	
Length-slow	Bundles of fibrous quartz length slow over entire length of fiber.	
Zebraic	Bundles of fibrous quartz which alternate length-fast and length-slow along length of fiber.	

Early observers of nodular cherts in limestones speculated that silica gels had precipitated directly from ocean water and transformed to quartz during burial. However, surface and shallow ocean waters today contain less than 1 mg/g silica due to efficient removal by silica-secreting diatoms. Therefore, direct precipi-tation of chert from modern ocean water does not occur.

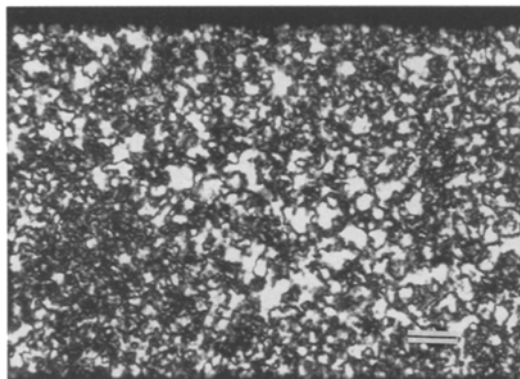
Prior to the mid-Tertiary explosion of diatom populations, it is likely that ocean water was held comparably low in dissolved silica by the abundant silica secreting radiolarians and sponges. The best argument for this is the fact that chert does not show up as part of Phanerozoic evaporite sequences. It is therefore unlikely that any of the Phanerozoic cherts were direct precipitates from ocean water. Precambrian cherts are more problematical; direct precipitations of opal or quartz from the Precambrian oceans may have occurred and may account for varieties that do not occur in the Phanerozoic (such as some chert beds in iron formations).



**Figure 1:** Diagenetic pathways for authigenic silica transformations. Granular microcrystalline quartz is the most common form of quartz in chert. In biogenic siliceous oozes, the initially precipitated opal-A dissolves and reprecipitates as opal-CT. Opal-CT subsequently dissolves and reprecipitates as microquartz. In platform carbonates, microquartz can directly replace limestone during early diagenesis. Other pathways are possible for other types of chert. Megaquartz can form as a direct precipitate from low temperature waters, or can be a metamorphic recrystallization of microquartz.

Tertiary deep ocean sediments contain extensive layers of biogenic siliceous oozes. Eocene radiolarian oozes are commonly encountered during deep sea drilling, and the Pacific basin is rimmed with Miocene diatomaceous deposits. Prompted by the Deep Sea Drilling Project and the demonstrated oil potential of the Miocene oozes, the most extensive efforts to understand silica diagenesis have been focused on these deposits. Studies have

repeatedly shown that siliceous oozes are initially laid down as biogenic opal-A and are then transformed during later burial to opal-CT and then quartz (Fig. 1). The bedded chert produced in this way is composed of quartz that formed during deep burial at temperatures up to 80°C, or higher. It can take more than 60 million years for the ooze to completely convert to quartz. Isotopic analyses of these types of chert yield information mainly about late diagenesis; determination of paleoclimatic temperatures is not possible unless it can be independently demonstrated that the transformation from opal to quartz occurred during shallow burial.



**Figure 2:** Photomicrograph of granular microcrystalline quartz in Cretaceous chert (Edwards Formation, Texas). Quartz grains are intergrown, have irregular extinction and irregular grain boundaries. Crossed nicols. Bar = 40 microns

Figure 1 gives alternative paths for the paragenesis of silica phases in sediments. The sequence deduced for the siliceous oozes does not necessarily apply to other types of cherts. Biogenic opal-A is coated with either metal oxides and/or organic matter to protect the opal from dissolving in sea water. This armoring greatly impedes the progress of silica transformations during burial. In addition, while pore fluids in siliceous oozes can achieve dissolved silica levels above the 80-120 mg/g values necessary for precipitation of opal-CT, this is rarely the case in other depositional settings. For example, ground waters moving through a carbonate unit may dissolve opaline tests or volcanic shards until the dissolved silica rises above 6 mg/g. At that

point, quartz can nucleate and grow without ever going through any intermediate phases.

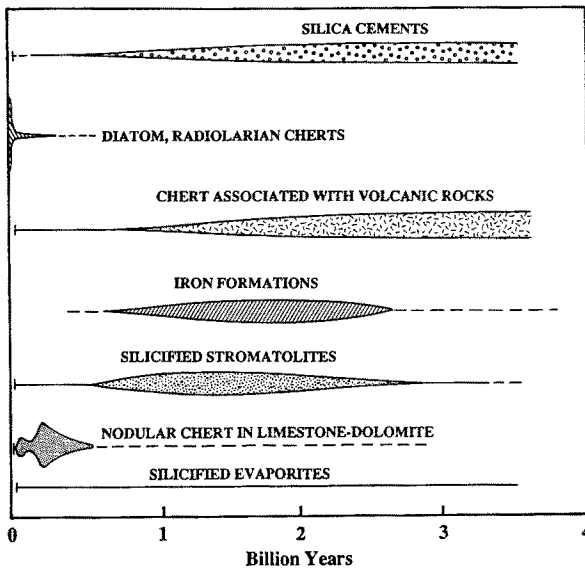
**Table 2**

OCCURRENCE	OPAL		Quartz				Marine	FW
	OPAL-A	OPAL-CT	OPAL-C	GMC*	Fibrous	Megaquartz		
Modern Organisms	x				?		x	x
Siliceous Oozes								
modern	x	?					x	x
ancient (Bedded Chert)		x		x	x	x	x	x
Nodular Chert in Carbonate								
Cenozoic	x	minor		x	x	x	x	x
Pre-Cenozoic				x	x	x	x	minor
Cherts Associated with Volcanic Rocks	x	?	x	x	x	x	x	x
Silicified wood	x	x		?	x	x		x
Iron Formations				x	x	x	?	?
Geodes					minor	x	?	x
Silica Cement								
Cenozoic	x	x		?	x	x	x	x
Pre-Cenozoic				?	x	x	x	x
Silicified Fossils								
Cenozoic	x	x		x	x	x	x	x
Pre-Cenozoic				x	x	x	x	x
Porcellanite (siliceous shales)				x			x	x
Inorganic Opal	x	x	x				?	x
"Magadii" cherts"	?	?		x	x	x		x
Silicified Erosion Surfaces	x		x	x	x	x		x
Fracture-Fills	x				x	x	x	x

\*GMC = Granular Microcrystalline Quartz

Cherts are most commonly composed of interlocking, intergrown grains of  $\alpha$ -quartz called granular microcrystalline quartz (micro-quartz). The grains average about 8 microns in size and display irregular extinction (Fig. 2). According to Micheelsen (1966), individual grains are made of plates about 600 angstroms thick and are stacked parallel to (0001). Each plate is the Brazil twin of the other and contains numerous lattice faults and dislocations studded with hydroxyl groups. Molecular water and hydroxyl also line the micro-plate surfaces. With time, this structure is probably annealed out and probably tends to approach more ordered grains of  $\alpha$ -quartz. However, many cherts as old as Archean have preserved their microquartz texture and are petrographically indistinguishable from cherts as young as the Cretaceous. Once formed, this intergrowth of quartz is highly impermeable and inert. Metamorphism can induce wholesale recrystallization into

larger, individual grains of  $\alpha$ -quartz with well defined grain boundaries and regular extinction called megaquartz. Simple petrographic examination can therefore readily delineate altered, metamorphosed chert from that which may be the original quartz precipitate. A more detailed discussion of silica phases and silica diagenesis is given in the useful review by Hesse (1989).



#### EVOLUTION OF AUTHIGENIC SILICA SYSTEM

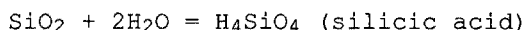
**Figure 3:** Evolution of authigenic silica associations with time. The width of the field for each chert type is a subjective impression of abundance during geologic time. The impression is based largely on the ease with which samples of each type can be obtained from the geologic column

Cherts are found in a number of different associations (Table 2). The paragenetic sequence of silica phases is not well known for most of these occurrences. Figure 3 gives an impression of the relative abundances of the major chert types over geologic time. Much of the variation is due to biological evolution. For example, the probable silica source of nodular cherts in limestones is siliceous sponges that co-existed with carbonate-secreting organisms. Such sponges were abundant in shallow platform sediments during the Paleozoic and Mesozoic, but are now abundant only in deep-sea settings. The near absence of nodular cherts in Neogene carbonates is probably due to the paucity of silica sponges in equivalent depositional environments that gave rise to

such a profusion of Paleozoic nodular cherts. The abundance of bedded cherts derived from Cenozoic siliceous oozes is likewise attributable to the Neogene explosion of diatoms.

#### OXYGEN ISOTOPE SYSTEMATICS

The basic dissolution-precipitation reaction for the silica-water system is:



At equilibrium, O atoms are continually exchanged back and forth between water molecules and  $\text{SiO}_2$  molecules via the mechanism shown. Isotopic fractionation should therefore occur and should be temperature dependent. It is important to note that isotope equilibration and exchange can occur only during events involving dissolution-precipitation of silica. If quartz simply recrystallizes without the addition or subtraction of  $\delta^{18}\text{O}$ , there will be no change in isotopic composition. For this reason, it is possible for cherts to be metamorphosed at high temperatures without undergoing any major change in  $\delta^{18}\text{O}$ , providing the water/rock ratio is low.

Quartz precipitates abundantly in sedimentary rocks, but the rate of precipitation is apparently too slow for meaningful laboratory synthesis at low temperatures. It has thus not been possible to calibrate the O isotope fractionation with temperature for quartz-water below  $200^\circ\text{C}$ . Various theoretical estimates and extrapolations from high temperature experiments have been made as summarized by Kyser (1987). Opal is readily synthesized, but the water content ranges up to 12 wt.% and cannot be easily removed without exchanging water O with the tetrahedrally bound silicate O. In addition, opal is amorphous and thus may not have Si-O bonding regular enough to yield systematic isotopic fractionation. The desired approach of grounding a method in theory, calibrating it in the lab, and then applying it to nature cannot yet be

applied to the silica system. However, the data for natural samples display many systematics that can be usefully and quantitatively interpreted.

The fractionation with temperature expression is probably approximated by a standard curve of the form:

$$1000\ln\alpha = A (10^6) (T^{-2}) + B \quad (T = ^\circ K)$$

If  $A = 3.09$  and  $B = -3.29$  (Knauth and Epstein, 1976), then this expression can be used to obtain geologically reasonable temperatures for cherts of all types over a broad range of diagenetic temperatures.

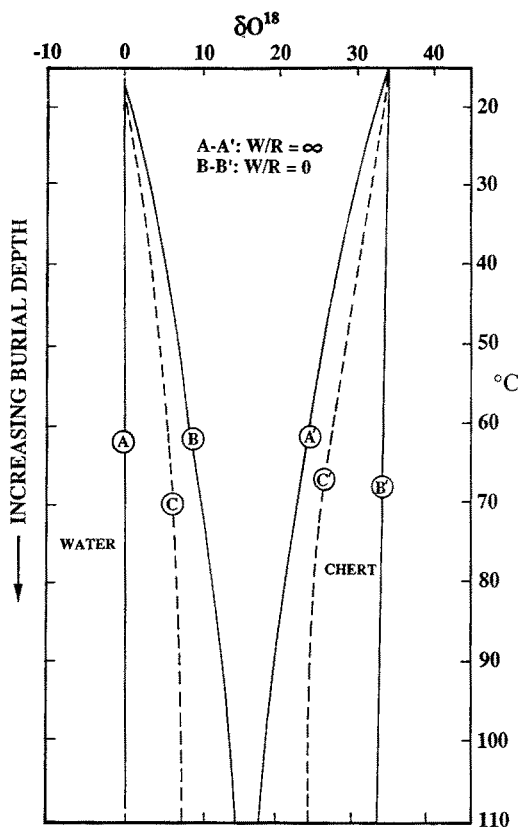
### Siliceous Oozes

The  $\delta^{18}O$  of marine diatoms and radiolarians is about +34 to +39 per mil, some of the most  $^{18}O$ -enriched material ever measured. Fairly pure layers of this material can range up to hundreds of meters thick in areas below the Carbonate Compensation Depth. Silica diagenesis may begin immediately upon burial, but substantial conversion into opal-CT may not occur until temperature rises above 45°C. In the typical case, the deep marine setting precludes entry of  $^{18}O$ -depleted meteoric waters into the sediments during diagenesis. The pore fluids are ocean water which can be expected to become slowly enriched in  $^{18}O$  by reequilibration with the  $^{18}O$ -enriched silica. The amount of the enrichment depends upon the water/rock ratio (W/R), defined as the atomic amount of O in the water divided by the atomic amount of O in the silica that equilibrates with this water.

At the sediment-water interface W/R approaches infinity, but the value must drop once the pore fluid is effectively cut off from the ocean reservoir. In the limiting case where there is little pore fluid, the sediment pile contains essentially all the O of the system. A tiny amount of water that equilibrates continuously with the silica as temperature increases will follow the curve for W/R = 0 shown in figure 4. In this case,  $^{18}O$  of the



sediment pile will not change because essentially all the O is in the silica. In the opposite limiting case where the amount of water is so great that essentially all the O of the system is in the pore water,  $^{18}\text{O}$  of the water will remain constant and  $^{18}\text{O}$  of the silica will decrease along the curve shown in the figure for  $W/R = \text{infinity}$ . Obviously, the natural situation will fall between the limiting values shown in figure 4. As the sediment pile compacts and dewateres, the  $W/R$  ratio will decrease and  $\delta^{18}\text{O}$  of water and silica will evolve along



**Figure 4:** Closed system isotopic equilibration of chert with water during increased burial/temperature as a function of water/rock ( $W/R$ ) ratio. When  $W/R$  is very low,  $\delta^{18}\text{O}$  of the sediment pile will not change (curve B'), and pore waters will become enriched in  $^{18}\text{O}$  along curve B. When  $W/R$  is very large, authigenic silica will precipitate along curve A'. Intermediate  $W/R$  ratios yield more realistic curves such as C-C'. A graph of this sort is most appropriate for diagenesis of deep sea siliceous oozes where intrusions of low- $^{18}\text{O}$  meteoric waters are unlikely, and the system can evolve as shown

intermediate values shown by the dashed curves in figure 4. The  $\delta^{18}\text{O}$  of opal-CT forming during burial can therefore be expected to be lower than  $\delta^{18}\text{O}$  of the precursor biogenic silica. Upon deeper burial, the opal-CT transforms to quartz and its  $\delta^{18}\text{O}$  can be expected to be lower still.

The general case of decreasing  $\delta^{18}\text{O}$  of deep sea diagenetic silica with increasing diagenetic grade has been observed in all cases examined so far. The  $\delta^{18}\text{O}$  values for opal-CT in core samples from buried deep sea oozes are always several per mil lower than co-existing remnants of the precursor biogenic silica. Quartz chert, which forms during deeper burial, is generally several per mil lower still (e.g. Kolodny and Epstein, 1976, and references cited therein). The same has been observed for the Miocene Monterey Formation, California, where diatomaceous oozes were buried to various depths and then rapidly uplifted along a tectonically active continental margin (e.g. Pisciotta, 1981).

Reliable temperature estimates based on  $\delta^{18}\text{O}$  of the opal-CT and/or quartz chert are not available because W/R and  $\delta^{18}\text{O}$  of the pore fluids are unknown. Indeed, much of the published work assumes  $\delta^{18}\text{O} = 0$  for the water throughout the burial history and the W/R ratio is rarely considered. In addition, silica diagenesis may locally proceed at greatly enhanced rates in response to controls not yet understood. For example, many black, "glassy", quartz cherts in the Monterey Formation have  $\delta^{18}\text{O}$  values above +28 per mil and cannot have formed at the 80°C temperature normally thought necessary to convert opal-CT to quartz. These are obviously an earlier generation of cherts that formed outside the normal burial diagenetic scheme of:

opal-A (biogenic silica) --> opal-CT --> Quartz.

This sequence is probably a limiting, general case upon which earlier transformations can be superimposed. Oxygen isotopes can be used to effectively determine which are the earlier (more  $^{18}\text{O}$  enriched) phases. If  $\delta^{18}\text{O}$  of the fluid can be measured or estimated, or if the W/R can be estimated, then actual tempe-

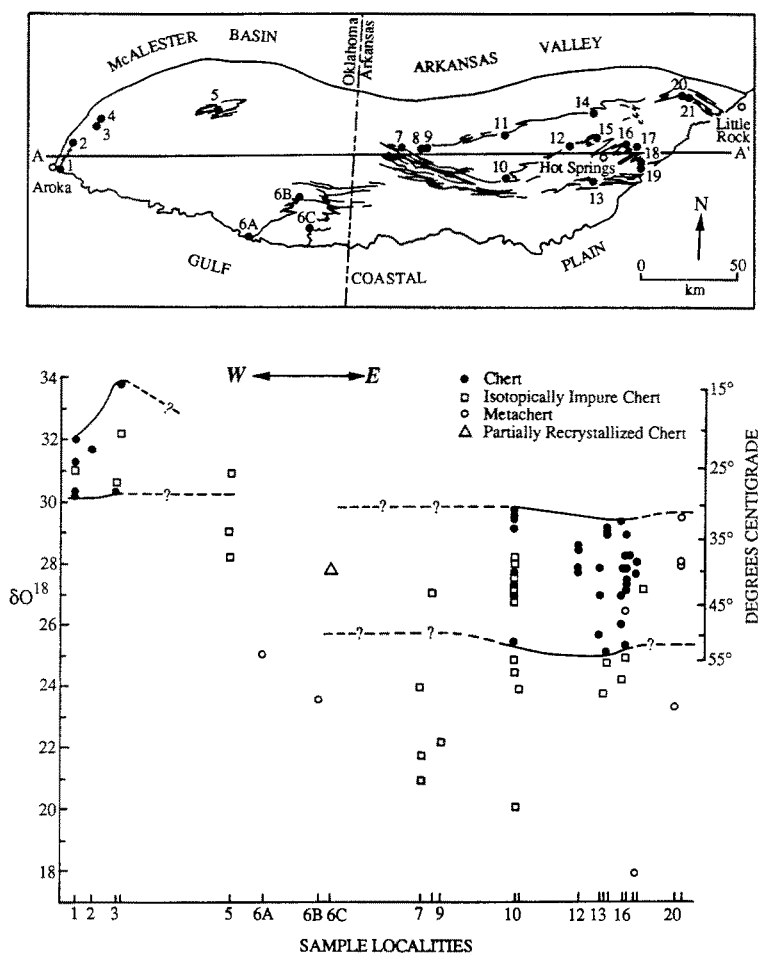
ratures can be estimated from a quantitatively constructed version of figure 4.

### Bedded Cherts

Siliceous oozes in various stages of conversion to quartz chert can be found throughout Tertiary sections, especially in deep sea settings. Subduction has largely removed the older oceanic crust, so the only remnants of ancient siliceous oozes are certain bedded cherts which have been deformed and accreted along ancient continental margins. These are generally radiolarian cherts and are found in Mesozoic and Paleozoic strata. These rocks are too old to contain any of the precursor phases; all opaline material has had sufficient time and/or temperature to convert to quartz. The Devonian Arkansas-Caballos Novaculite of Arkansas, Oklahoma, and Texas is a famous example.

Jones and Knauth (1979) analyzed numerous samples of the novaculite in Arkansas. A wide range of  $\delta^{18}\text{O}$  values was observed (Fig. 5). Most of the variation was attributed to chert crystallization at various burial depths. In places the novaculite has been strongly metamorphosed. During regional metamorphism temperatures could rise to more than  $300^\circ\text{C}$ . At this temperature, the fractionation between quartz and water is less than 6 per mil. The  $\delta^{18}\text{O}$  of metachert will depend upon  $\delta^{18}\text{O}$  of the metamorphic fluid, the W/R ratio, and the degree to which the fluid circulates through the region (thereby allowing it to exchange with rocks of different  $\delta^{18}\text{O}$ ). The general effect is that  $\delta^{18}\text{O}$  of the chert tends to decrease. However, unless a large amount of fluid is circulated throughout the chert beds,  $\delta^{18}\text{O}$  of the chert will not be significantly lowered. For example, if  $T = 300^\circ\text{C}$  and W/R is near zero, the water will simply equilibrate with the chert to a  $\delta^{18}\text{O}$  value about 6 per mil lower than the chert. As the chert recrystallizes, the water will move through the rocks and continually reequilibrate with the chert. However, neither the water or the chert will be further altered isotopically; the reservoir of O is in the rock and there is insufficient water to add or subtract  $^{18}\text{O}$  from it. Jones and Knauth (1979) argued that

regional metamorphism of the Arkansas bedded cherts had lowered  $\delta^{18}\text{O}$  of the chert by 0 to 7 per mil. Many recrystallized cherts were isotopically similar to unmetamorphosed examples from the same terrane. Metamorphism under relatively dry conditions is implied. The most extreme lowering was for a contact metamorphosed sample which has been lowered to a  $\delta^{18}\text{O}$  value of +18 per mil.



**Figure 5:**  $\delta^{18}\text{O}$  of Devonian Novaculite, a bedded chert produced by diagenesis of a siliceous ooze. Outcrop and localities are in the top part. Sample localities are projected on line A-A' and plotted against  $\delta^{18}\text{O}$  in the bottom half. Varied  $\delta^{18}\text{O}$  values at each locality are interpreted as microquartz crystallization at various depths. Cherts on the western side are enriched in  $^{18}\text{O}$  relative to the eastern side, indicating precipitation at shallower burial depth. Recrystallized cherts are not strongly depleted in  $^{18}\text{O}$  indicating that metamorphic W/R ratios were low (From Jones and Knauth, 1979)

In general, bedded cherts found in Phanerozoic eugeosynclinal sequences probably originated as radiolarian oozes. Oxygen isotope variations for bedded chert samples composed of microquartz are probably caused by crystallization at various burial depths. Megaquartz samples have  $\delta^{18}\text{O}$  values related to metamorphic reequilibration of precursor microquartz, but these values are not necessarily much lower than those of the original chert.

#### Magadi-Type Cherts

The world's youngest cherts are found in Lake Magadi, Kenya, and have been thoroughly described by Eugster (1969). Lake Magadi is located in the rift valley of East Africa and contains an alkaline lake perched within young volcanic rocks. Eugster proposed that Na is leached out of an authigenic hydrous Na-silicate phase by meteoric waters to produce hydrous Si which then becomes chert. However, O'Neil and Hay (1973) found that  $\delta^{18}\text{O}$  of the chert ranged from +31 to +44.1 per mil. The +44 values are probably the heaviest terrestrial  $\delta^{18}\text{O}$  values ever measured and are hard to reconcile with leaching by meteoric waters. If Eugster is correct, then the original Na silicate was an  $^{18}\text{O}$ -enriched evaporite phase which was somehow subsequently leached free of Na by meteoric fluids without O isotopic exchange. An alternative is that many cherts in Lake Magadi simply precipitate during seasonal evaporation, and that these were the types of cherts analyzed by O'Neil and Hay (1973). In any case, Magadi cherts are unusual and probably will not be encountered often in the geologic record. They are most likely to have occurred in interior basin deposits.

#### Cherts in Iron Formations

Throughout much of the Precambrian, cherts are found interbedded with layers of Fe oxide and/or siderite. The origin of iron formations remains one of the most perplexing problems in geology, and many explanations have been offered for these remarkable rocks. Most have been metamorphosed, and the diagenetic sequence that gave rise to quartz chert cannot yet be specified.

Quartz may have been a primary precipitate from the oceans or it could be a transformation product of precursor opaline phases. This question is of profound importance in interpreting  $\delta^{18}\text{O}$  data. Do the data tell us about the initial sedimentation, early diagenesis, deep burial diagenesis, or only metamorphism?

The most extensive study was done for the Brockman Iron Formation in Australia by Becker and Clayton (1976). They measured  $\delta^{18}\text{O}$  of co-existing quartz and magnetite and concluded that the phases had equilibrated at temperatures approaching  $350^\circ\text{C}$ . The  $\delta^{18}\text{O}$  of the quartz was about +21 to +22 per mil. These are much lower  $\delta$ -values than observed for typical Phanerozoic cherts. One possible reason for this is that the quartz was preceded by more  $^{18}\text{O}$ -enriched opaline precursors, and then lowered wholesale during metamorphism (Becker and Clayton, 1976). Alternatively, the relative amount of silica may have been so large that little  $^{18}\text{O}$  was added or subtracted by metamorphic fluids and that the quartz today is little different from the primary values. The low  $\delta^{18}\text{O}$  can then be alternatively explained in terms of higher Precambrian temperatures, lower  $\delta^{18}\text{O}$  of the oceans, or input of low  $^{18}\text{O}$  meteoric waters into the original sedimentary basin.

Unlike the Brockman Iron Formation, quartz in the Gunflint Iron Formation displays a large variation in  $\delta^{18}\text{O}$ . This quartz occurs interbedded with iron oxides, siderite, and replaces stromatolites and limestone, all in a bewildering variety of petrographic textures. Unpublished  $\delta^{18}\text{O}$  values range from +17 to +26 per mil. Metamorphism is locally the cause of some of this variation, but interpretations of the data are still preliminary. The isotopic investigation of iron formations is still in its infancy. It is clear that many examples are likely to display large variations in  $\delta^{18}\text{O}$ , and this will undoubtedly be useful in understanding the origin(s) of these important rocks.

#### Nodular cherts

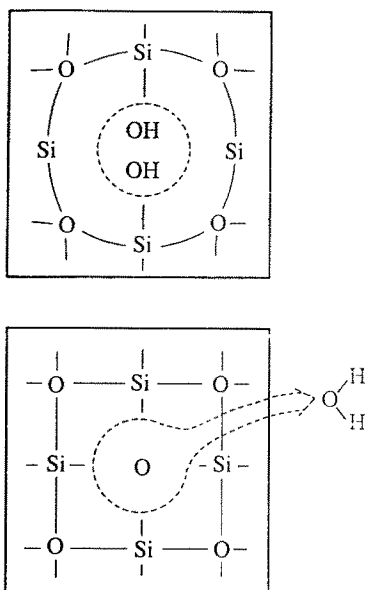
Nodules, thin beds, stringers, and irregular accumulations of quartz chert occur in carbonate rocks ranging from Archean to

Miocene time. In Phanerozoic rocks this chert occurs in limestones and dolostones. In Precambrian rocks it occurs in stromatolitic carbonates, but some is also found in siderite beds associated with iron formations. The outlines of former spicules are common in most Phanerozoic examples (best seen on wet fractured surfaces with a hand lens), and it is likely that sponges were the source of silica. A typical platform carbonate deposit probably consisted originally of aragonite and high-Mg calcite shell debris together with abundant sponge spicules of opal-A. During early diagenesis, the metastable carbonate phases were converted to low-Mg calcite and/or dolomite. At some point during this "stabilization" episode the biogenic silica was mobilized and reprecipitated into quartz chert. The timing of silicification was variable, but good arguments can be made that it was typically pre-compaction of the sediments, prior to most dolomitization, and before loss of significant permeability.

The chert typically replaces the metastable carbonate phases on a fine scale; fossils and early sedimentary textures are often remarkably well preserved inside cherts. Even the youngest Tertiary nodular cherts are composed of microquartz. While opal-CT may, in some cases, precede quartz precipitation, it appears that quartz was typically the primary precipitate. It is likely that the diagenetic fluids were saturated with respect to quartz, but rarely rose to the 80 mg/g values necessary for opal-CT precipitation. Vugs and dissolution cavities are often filled with fibrous quartz and drusy quartz, but many of these may relate to later subaerial exposure events that are being increasingly recognized in ancient, epeiric sea platform carbonates. Isotopic analyses of microquartz probably yield information about the earliest diagenetic events. Samples laced with fibrous quartz and megaquartz vug-fills yield  $\delta$ -values that are harder to interpret because this material can fill void spaces at any time in the burial-uplift history of the unit.

The water content in nodular cherts ranges downward from about 1 wt.% and averages about 0.5 wt.%. In older cherts, any original hydroxyl bonded to Si has very likely changed into molecular H<sub>2</sub>O via the mechanism shown in figure 6. The H<sub>2</sub>O may escape, remain

trapped as isolated molecules at dislocations, or combine with other  $\text{H}_2\text{O}$  molecules to form fluid inclusions. Fluid inclusions of the original water in which the chert precipitated may also be present. Water extracted from cherts may therefore have the combined  $\delta\text{D}$  values of the primary diagenetic fluid and fractionated water that was originally bonded as hydroxyl. The hydroxyl in cherts is probably depleted in D by 20-50 per mil relative to the water in which the chert forms because this is the magnitude of the  $\text{OH-H}_2\text{O}$  fractionation in clay minerals.

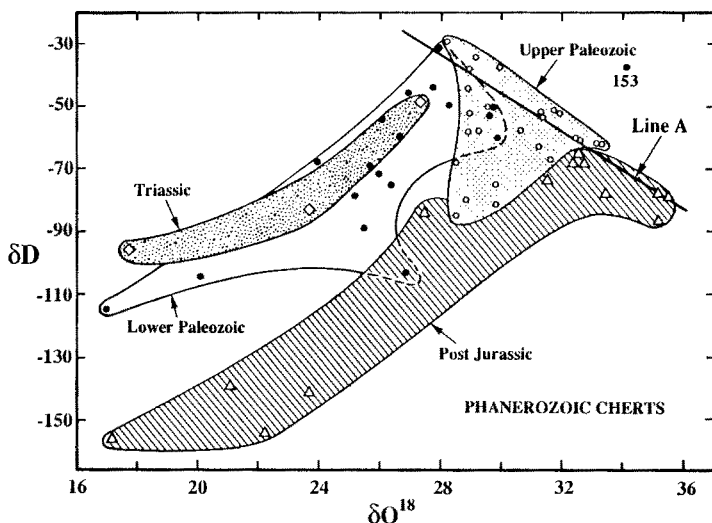


**Figure 6:** Dehydration of hydrous silica. Two hydroxyls can combine to produce  $\text{H}_2\text{O}$ . One hydroxyl O is left behind to Si, thereby annealing out the former defect. The  $\text{H}_2\text{O}$  may leave the system, or collect with other  $\text{H}_2\text{O}$  molecules into a tiny fluid inclusion.  $\delta\text{D}$  of this water is determined by the hydroxyl fractionation of the original precipitate

Figure 7 shows combined  $\delta\text{D}-\delta^{18}\text{O}$  measurements for cherts of various ages. The  $\delta^{18}\text{O}$  is for the silicate O and  $\delta\text{D}$  is for water extracted by dehydration at  $1000^\circ\text{C}$  under vacuum. Most of the samples are nodular cherts in carbonates. Cherts within specified age limits yield domains of  $\delta$ -values which are stretched out roughly parallel to the meteoric water line. In Knauth and Epstein's (1976) interpretation the cherts can be treated similar to the clay minerals;  $^{18}\text{O}$  is preferentially concentrated during precipitation into the silica and D is preferentially excluded



from the hydroxyl. On a  $\delta D$ - $\delta^{18}O$  diagram, chert data therefore plot to the lower right of the water with which they last equilibrated.



**Figure 7:**  $\delta D$ - $\delta^{18}O$  of Phanerozoic cherts in carbonates. The data for selected age groups are elongated parallel to the meteoric water line. The shift of the elongated domains toward and away from the meteoric water line with time can be interpreted in terms of large changes in climatic temperatures over geologic time. The "cut-off" in  $\delta$ -values to the upper right is understood if line A is the approximate locus of  $\delta$ -values for cherts in isotopic equilibrium with sea water. The lower  $\delta$ -values reflect original precipitation of chert in mixed marine-meteoric diagenetic waters (From Knauth and Epstein, 1976)

The maximum  $\delta$ -values for cherts of various ages appear to approach a limit, shown as line A in figure 7. Line A is interpreted as the trajectory on a  $\delta D$ - $\delta^{18}O$  diagram that chert will take as it equilibrates with ocean water (approximated by SMOW) at various temperatures. In coastal diagenetic environments  $\delta$ -values for the groundwaters will decrease landward as lighter meteoric waters are mixed with marine waters. Cherts which form in mixed marine-meteoric fluids at a constant temperature will plot progressively farther away from line A in proportion to the magnitude of the light meteoric water component. An individual line parallel to the meteoric water line should result for cherts which form at the same temperature. For these reasons, Knauth and Epstein (1976) argued that cherts of the various ages shown had

formed at various temperatures in mixed meteoric-marine diagenetic fluids. Those plotting nearest line A were those which contained the greatest marine component. The scatter within a domain probably arises because of temperature variations during the time shown and because some water is derived from submicroscopic fluid inclusions containing unfractionated remnants of the original diagenetic fluid. Additionally, pyrolysis of trace amounts of organic matter in the chert occurs during sample heating, and this yields water which contaminates the silica water.

Cherts of various ages plot in different positions on this diagram, and this can be interpreted in several ways. If ocean water was isotopically different in the past, then the position of the meteoric water line would also be different. Thus, if the oceans were several per mil depleted in  $^{18}\text{O}$  in the Cambrian relative to the upper Paleozoic, then the domain of chert  $\delta$ -values could be concomitantly displaced as shown (assuming that the range of precipitation temperatures was similar). However, large changes in  $\delta^{18}\text{O}$  of ocean water are required between the Upper Paleozoic and the Triassic (-4 per mil) and between the Triassic and the Miocene (+6 per mil) to explain the data in terms of changes in the isotopic history of sea water. Such large changes are improbable.

The average ground temperature below a few meters depth is an excellent average of the yearly climatic temperature, so temperatures deduced for nodular cherts that formed during early diagenesis should approximate climatic temperatures. Temperatures can be assigned to line A by using one of the quartz-water  $\text{O}$  isotope fractionation curves and assuming that  $\delta^{18}\text{O}$  of pre-Pleistocene ocean water was approximately -1 per mil (the value for an ice-free world). Parallels to the meteoric water line which pass through the data domains can be determined from their intersection point on line A. Temperatures assigned in this way are obviously approximate. Knauth and Epstein (1976) argued that climatic temperature variations accounted for the major part of the variations shown in figure 7, and suggested that climatic temperatures decreased from Cambrian values on the order of  $34^{\circ}\text{C}$  to Upper Paleozoic values of  $20^{\circ}\text{C}$ . The Triassic returned to temperatures similar to those of the Cambrian and then declined to

Miocene values of 17°C. A few Precambrian values (not shown in Fig. 7) are also variable, and range from values similar to those of the Upper Paleozoic to as high as 70°C in the Archean. The chert-water O isotope fractionation with temperature equation of Knauth and Epstein (1976) was estimated, in part, on trial-and-error fits to line A that would yield reasonable temperatures. The actual temperatures are therefore not rigorous, but temperature differences between different ages are similar no matter which quartz-water temperature-fractionation expression is used.

Hydrogen isotopic analysis of cherts has not been extensively used. Organic matter and clay minerals are ubiquitous contaminants and many workers are reluctant to accept that small amounts of water can remain isotopically unaltered in cherts over geologic time. The amount of water is so small that any external fluids which penetrate the sample could obliterate the record and any recrystallization during metamorphism or hydrothermal alteration could profoundly affect  $\delta D$ . Nevertheless, the  $\delta D$  data for cherts of a given age tend to vary sympathetically with  $\delta^{18}O$ . Careful analyses of samples screened for purity and textural preservation appear to be meaningful. A further refinement is possible in which the constituent petrographic phases are separated and analyzed; previous analyses have generally been for coarse separates or whole rocks. Even if the H data are accepted, it has not been resolved how the data in figure 7 are best interpreted. The climatic temperature variations are larger than many are willing to accept. However, the fossil record does not provide a strong constraint on actual temperatures. Many modern organisms thrive in the higher temperature range suggested for the Phanerozoic, and the blue-green algae (cyanobacteria) that make up the predominant fossils of the Precambrian are today found growing in abundance in hot springs at temperatures even warmer than the maximum suggested value of 70°C.

The strong indications that meteoric waters were involved in chert diagenesis in marine carbonate rocks prompted Knauth (1979) to propose a coastal mixing zone model for the origin of chert in limestone which explains many geochemical, petrographic, and field data for such cherts. Kolodny et al. (1980) have given independent

arguments based on  $\delta^{18}\text{O}$  and B geochemistry that meteoric waters were involved in the formation of nodular cherts in limestones. These arguments are independent of considerations involving H isotopes. Relative changes in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  will likely prove increasingly useful in unravelling silicification sequences within individual carbonate units.

#### An Application: $\delta^{18}\text{O}$ of Cherts versus Time

The first isotopic investigation of cherts was by Degens and Epstein (1962). They observed that  $\delta^{18}\text{O}$  for cherts generally decreases for progressively older samples, just as it does for limestones. At the time, it was assumed that limestones slowly equilibrate with later,  $^{18}\text{O}$ -depleted groundwaters. Therefore, the older the sample, the more time there was for exchange and the lighter was the calcite. Since the chert data paralleled the carbonate data, it was concluded that the cherts had also lost their isotopic memory.

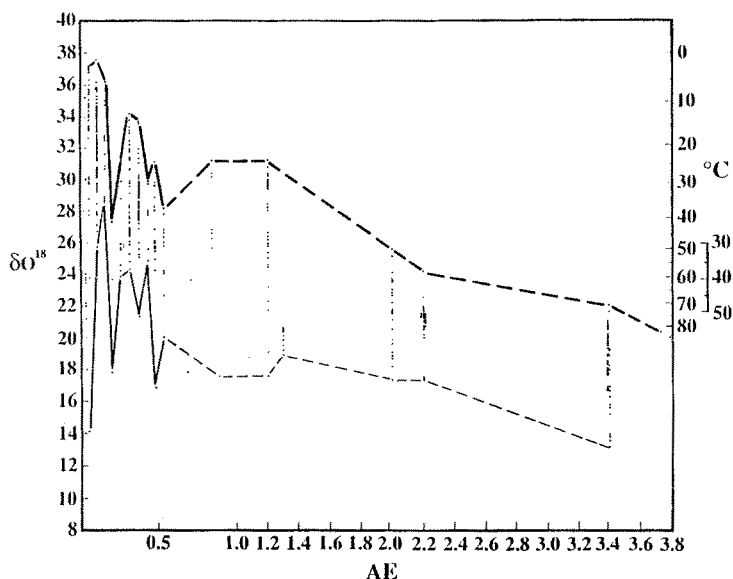
Perry (1967) analyzed samples from thick, bedded chert sequences and observed that  $\delta^{18}\text{O}$  for these trended back through geologic time along a different trajectory than that observed by Degens and Epstein (1962). He suggested that his cherts had preserved their  $\delta^{18}\text{O}$  values from the time of deposition and that these could be used to infer important information about earth history. His Precambrian samples had  $\delta^{18}\text{O}$  as low as +14.1 per mil, and Perry argued that this could not be a temperature effect because the temperatures would be unreasonably high. He suggested that  $\delta^{18}\text{O}$  of the Archean ocean was 18 per mil lower than the modern ocean and that the oceans had become progressively enriched in  $^{18}\text{O}$  as recorded by the cherts. This important and provocative paper called attention to the possibility of a rich isotopic record in ancient sedimentary rocks; a record that contained important information about earth history. Figure 8 shows a compilation of  $\delta^{18}\text{O}$  measurements of cherts over geologic time. All of these data have been obtained since Perry's (1967) original paper. The data are generally heavier than Perry's original values, and this has reopened the possibility that climatic

temperature variations are largely responsible for the lower  $\delta^{18}\text{O}$  values in the past.

It now appears that cherts can be expected to have a wide range of initial  $\delta^{18}\text{O}$  values that vary with the conditions of formation. In deep sea cherts and other varieties that have opaline precursors, the final quartz may form over a range of burial temperatures and thus have  $\delta^{18}\text{O}$  values ranging from relatively heavy, low temperature values to relatively light, higher temperature values. In nodular cherts which form in platform carbonates, the chert may form before significant burial at a relatively constant temperature, but a large range in  $\delta^{18}\text{O}$  may result because variable amounts of low- $^{18}\text{O}$  meteoric waters are involved. For older cherts, metamorphism may further lower  $\delta^{18}\text{O}$  by exchange at elevated temperatures. Thus, it is the maximum  $\delta^{18}\text{O}$  for cherts of a given age that is of most importance. This is the  $\delta$ -value that would most closely correspond to hypothetical chert that formed in sea water, and is the most useful value for monitoring either changes in  $\delta^{18}\text{O}$  of the past oceans or past climatic temperatures. Of course, in evaporite environments  $\delta^{18}\text{O}$  of the water can rise above marine values as the lighter isotopes are preferentially removed. However, evaporite cherts appear to be rare, and the odd case can usually be recognized in compilations of large amounts of data.

The temperature scale in figure 8 is for the case where  $\delta^{18}\text{O}$  of the ocean is held at -1 per mil over geologic time and is based on the chert-water fractionation with temperature expression of Knauth and Epstein (1976). In this interpretation, the early earth may have been as hot as  $70^\circ\text{C}$ . By 1.2 Ga b.p. temperatures decreased to lower than  $30^\circ\text{C}$ , increased by about  $10^\circ\text{C}$  around Cambrian time, and generally decreased throughout the Paleozoic. Temperatures rose in the Triassic and declined to values shown for the mid-Tertiary. These are similar to temperatures deduced from the combined H and O isotope data, but this interpretation does not depend upon  $\delta\text{D}$  and the additional uncertainties associated with that measurement. Nearly all of the post-Archean data are from North America and are for cherts that undoubtedly formed at various latitudes. However, surface temperature variations with

latitude are greatly reduced in an ice-free world, and may amount to less than 10°C between the equator and 60° latitude (cf. Barron and Washington, 1985; Fig. 1). It is therefore unlikely that the large variations shown are caused by different paleolatitudes of the samples. There are other concerns about interpreting the chert data purely in terms of temperature, but this remains the simplest interpretation for the major part of the variations shown.



**Figure 8:** Changes in  $\delta^{18}\text{O}$  of cherts with time. Phanerozoic data are mostly from nodular cherts in carbonates, but also include bedded cherts. Precambrian data are from silicified stromatolites, but also include iron formation cherts and cherts of uncertain origin. Cherts known to be altered by metamorphism have been omitted. At any given age the large range of  $\delta^{18}\text{O}$  values is due to variable amounts of meteoric water involved in chert precipitation, crystallization at different burial depths and post-depositional lowering of  $\delta^{18}\text{O}$  during metamorphism. The high  $\delta^{18}\text{O}$  at any age best approximates  $\delta^{18}\text{O}$  of chert in isotopic equilibrium with sea water. Assuming that  $\delta^{18}\text{O}$  of sea water was approximately constant at -1 per mil, "surface" temperature variations over earth history are reflected by changes in the upper bound to the data and can be estimated by temperature scale (0-80°C) given on the right. The lower data may reflect the range of meteoric water  $\delta^{18}\text{O}$  that exist at a given time, a function of climatic temperatures and  $\delta^{18}\text{O}$  of the oceans. The strong  $^{18}\text{O}$  depletions for the earliest cherts suggest that sea water at 3.5 AE was several per mil lower than its value over most of the time. The 30-50°C temperature range shown at the right is for  $\delta^{18}\text{O}$  of sea water = -2. According to these interpretations, Archean surface temperatures may have been as high as 50-70°C

The lower curve brackets the minimum  $\delta^{18}\text{O}$  values and these values may be of some significance. If the variation of  $\delta^{18}\text{O}$  for unrecrystallized nodular cherts of a given age is largely due to the amount of meteoric water involved in silica diagenesis, then the minimum value for the cherts is also sensitive to changes in  $\delta^{18}\text{O}$  of the past oceans. It is therefore noteworthy that the minimum  $\delta^{18}\text{O}$  is roughly constant at about +18 per mil except for a number of Archean samples. This may be telling us that the Archean ocean was several per mil lower in  $\delta^{18}\text{O}$  and the temperatures would then reduce by 15–20°C. These reduced values still indicate much warmer Archean climates. Of course, it is possible that the minimum  $\delta$ -values are simply for the more deeply buried or metamorphosed cherts and put no constraints on the overall interpretation. More data for unrecrystallized low  $^{18}\text{O}$  cherts are clearly needed.

An additional explanation for the low  $^{18}\text{O}$  Archean cherts is that they precipitated from hot fluids circulating around mid-ocean spreading centers. Paris et al. (1985) have suggested such a setting for the South African cherts which make up the bulk of the Archean data shown in figure 8. The entire Onverwacht-Fig Tree sequence is silicified on a scale unknown in younger sedimentary rocks. This could support the arguments of Paris et al. (1985), or it could simply mean that surface temperatures were as hot as suggested above, and that the earth's surface was essentially an open hydrothermal system in the Archean.

## OTHER ISOTOPE SYSTEMATICS

### Silicon

The masses of the three stable Si isotopes ( $^{28}\text{Si}$ ,  $^{29}\text{Si}$ ,  $^{30}\text{Si}$ ) are too heavy for large fractionation effects, but the occurrence of Si in terrestrial rocks is so widespread that several attempts have been made to measure natural variations in its isotopic composition. The most recent survey (Douthitt, 1982) confirms that

$^{30}\text{Si}/^{28}\text{Si}$  varies by about 1 per mil for igneous rocks, but varies by several per mil for low temperature silica. Opal from both sponge spicules and siliceous sinters (opal deposited around hot springs) is about 2 per mil depleted in  $^{30}\text{Si}$  relative to the igneous rocks, while opal phytoliths are about 3 per mil enriched. Cherts display a 3.1 per mil variation centered around igneous rock values.

Douthitt (1982) suggested a kinetic isotope fractionation for the rapidly-precipitated siliceous sinter and for biogenic silica precipitation. Since the cherts do not display the Si isotope variations of their supposed biogenic precursors, it was suggested that the silica re-equilibrates with dissolved Si of normal isotopic composition during the conversion to quartz. Si isotope variations appear to be of marginal use in understanding chert diagenesis, but the previous work has been very limited. An investigation of cherts of various types and various ages using extremely accurate measurements might yet prove useful.

#### Lead, Neodymium and Strontium

Extremely pure domains of  $\text{SiO}_2$  probably exist in most cherts and opal deposits, but examination of thin sections readily reveals impurities in every example. The impurities can include carbonate, clay, micas, feldspar, organic matter, fluid inclusions, and a variety of terrigenous debris. These impurities occur in trace amounts in the purest cherts, but can be the major phases in some samples. Chemical analyses of cherts typically relate to these impurities rather than to atomic substitutions within the quartz crystals or opaline domains themselves. The low temperature  $\text{SiO}_2$  structure contains dislocations, is variably ordered on the long range, and may be quite inflated relative to the quartz of mineralogy books. Atomic substitutions not normally thought possible for quartz may be a reality in some forms of chert and opal. Detailed microprobe analyses of micron sized areas have not been reported, and the crystal chemistry of low temperature silica is largely unknown. Heavy isotope studies of cherts involve whole rock samples and thus relate primarily to the impurities rather



than the  $\text{SiO}_2$  itself. The extent to which such studies of impurities yield information about silica diagenesis must be evaluated for each individual case.

Barrett (1980) interpreted Pb isotopes in a sequence of Jurassic radiolarian cherts overlying ophiolites in terms of a mixture of continentally and mantle derived Pb. The cherts immediately overlying the basement are rich in volcanogenic Pb which was laterally dispersed from an active ridge. As the area was progressively blanketed with radiolarian ooze the amount of volcanogenic Pb decreased relative to the amount of radiogenic Pb provided by fine-grained terrigenous detritus. A stratigraphy of upwardly decreasing mantle Pb is thus preserved in the chert layers. The Pb isotope reservoir at the time of deposition was preserved when the siliceous ooze transformed to chert. Many ancient cherts are of problematic origin and hydrothermal activity associated with basaltic volcanism is often proposed as a silica source. The Pb isotopes appear to be a potentially useful approach for evaluating such situations, but the method is largely unexploited.

Sm-Nd systematics are similarly promising for tracing initial environmental conditions of cherts. Weis and Wasserburg (1987a) showed that oceanic cherts that form far from terrigenous source areas have impurities (carbonate?) with Nd isotopes characteristic of the ocean they form in. Others that form near continents have Sm/Nd ratios typical of continental sources. Sm-Nd systematics are incredibly sensitive to source terranes; even modern Atlantic ocean water is different from its Pacific counterpart. The possibilities are good that cherts encase a detailed Nd isotopic record that could be put to great use.

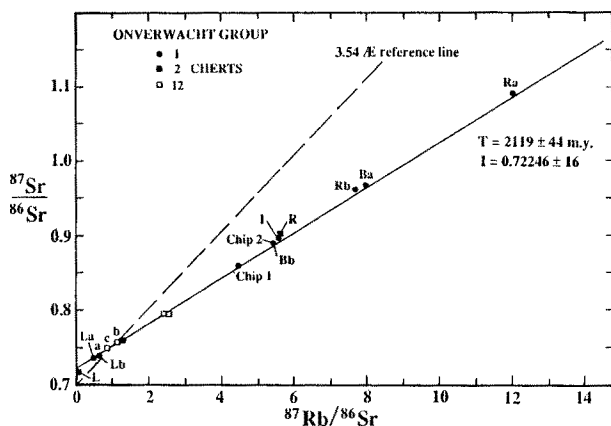
The Rb-Sr method holds promise for age dating some types of chert. Weis and Wasserburg (1987a) have shown that Rb is strongly enriched relative to Sr in most forms of biogenic silica and in selected chert samples. The enrichment of Rb over Sr is so large that measurable variations are likely in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios due to  $^{87}\text{Rb}$  decay. The site of the Rb is unknown, but is probably associated with impurity phases rather than with the  $\text{SiO}_2$  itself.

The Rb-Sr age dating method can be applied for situations where the chert encases impurities with the same  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (such as unaltered marine carbonate), or where exchange between impurities and diagenetic fluids homogenizes the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios prior to being sealed up by chert precipitation.

Siliceous oozes that accumulate far from land should contain only marine authigenic phases such as carbonate, zeolite, or smectite. The Sr in these phases should have the same  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio as sea water. This has been documented for a mid-Pacific chert sample dredged from an outcropping Eocene carbonate horizon on the flanks of a guyot (Weis and Wasserburg, 1987a). Siliceous oozes which accumulate nearer to land contain terrigenous clays carrying radiogenic Sr from their continental source areas. These will yield data scatter or mixing lines on a Rb-Sr evolution diagram. There is some evidence that  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the various impurity phases can become homogenized by interaction with pore fluids during deep burial of siliceous oozes prior to the depth at which opal-CT forms (Brueckner and Snyder, 1985). For such cases, Rb-Sr isotope analyses may yield the age at which opal-A converted to opal-CT during deep burial. Similarly, Shibata and Mizutani (1982) obtained whole-rock Rb-Sr isotope ages for quartz cherts in the Triassic of Japan which are 15 million years younger than the biostratigraphic ages. They suggested that these cherts originated during deep burial diagenesis of a siliceous ooze, and that the radiometric age was the time at which the quartz became a chemically closed system.

Several attempts have been made to date the world's oldest cherts in the Onverwacht Group, S. Africa. Hurley et al. (1972) obtained a Rb-Sr isochron which gave an age of 3.5 Ga, consistent with ages for the more readily datable crystalline rocks associated with the Onverwacht sequence. Weis and Wasserburg (1987b) suggested that Hurley et al.'s linear array was, instead, a mixing curve caused by variations in the amount of carbonate and muscovite in the samples. They obtained a Rb-Sr age of 2.12 Ga which they argued was the age of a previously unrecognized metamorphic event that recrystallized the Onverwacht cherts (Fig. 9). This result raises interesting questions about just when the

geochemical signatures, including  $\delta^{18}\text{O}$ , were locked into these ancient samples. Can Sr isotopes in the muscovite and carbonate impurities in these cherts be homogenized during metamorphism without wholesale exchange of the O isotopes? How much of the early diagenetic isotope record can be read through the later events that had 3.5 Ga to occur? In dealing with Archean sedimentary rocks, the questions of metamorphic overprinting are critical; satisfactory answers will require integrated field, petrographic, and isotopic studies on a scale not yet attempted.



**Figure 9:**  $^{87}\text{Rb}$ - $^{87}\text{Sr}$  evolution diagram for cherts from the Onverwacht Group, South Africa. The letters B, L and R stand for bulk, leach, and residue. The letters a, b, and c correspond to different layers in sample 12. An additional sample plotting off the diagram has been used in the age and initial ratio calculation (After Weis and Wasserburg, 1987b)

## CONCLUSION

Most previous isotopic work on cherts has involved broad surveys of limited numbers of chert types. Much emphasis has been given to the diagenesis of siliceous oozes, but these deposits are not generally representative of the cherts encountered in the pre-Mesozoic sedimentary record. Chert forms in siliceous oozes long after original deposition of the original, precursor biogenic opal, and isotopic studies of these cherts yields information primarily about deep burial diagenesis. The common nodular cherts

in carbonates of all ages are typically early replacements of original carbonate and may not follow the paragenetic sequence known so well for siliceous oozes. Isotopic studies of these cherts may yield environmental information, including climatic temperatures and the meteoric/marine nature of early diagenetic fluids. Other chert types, including those associated with the abundant Precambrian iron formations, are poorly understood; results for siliceous oozes and nodular cherts may not apply to these rocks. Most of the older chert sequences have been metamorphosed to various degrees. Isotopic variations of these rocks may yield information only about conditions of metamorphism or they may remain unaltered in cases where the water/rock ratio was low. The large O isotopic variations in cherts of a given age are therefore due to quartz crystallization at various burial depths, variations in the amount of low- $^{18}\text{O}$  meteoric waters in the diagenetic fluids, and lowering of  $\delta^{18}\text{O}$  during metamorphism.

Water can be extracted from almost any chert, and its  $\delta\text{D}$  often varies sympathetically with  $\delta^{18}\text{O}$  of the host silica. Combined  $\delta\text{D}$ - $\delta^{18}\text{O}$  analyses of nodular cherts in carbonates can be used to infer both temperature of formation and the relative amount of meteoric water that was present in the diagenetic fluid. Archean cherts are substantially depleted in  $^{18}\text{O}$  relative to Phanerozoic examples. The variation of  $\delta^{18}\text{O}$  of cherts over geologic time is not clearly understood, but much of it can probably be attributed to major changes in past climatic temperatures.

The Si isotopes vary little in terrestrial rocks, but the largest known effects have been observed in certain forms of opal. The isotopes of heavier elements are located in impurity phases in the silica and can be used as tracers and possibly as age indicators. Because of the large isotopic variations and the diversity of chert types, it is likely that isotopic analyses of cherts will be increasingly used, not only to better understand the chert problem, but to attack broader problems associated with the sedimentary sequences in which authigenic silica is found.

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