Glass ionomers have been a part of dentistry officially since 1972. However, they were, for all practical purposes, a derivation of the earlier silicate cements. Alan D. Wilson (a government chemist in England) guided the transition from silicates to glass ionomers. Throughout the following presentations, we will jump back and forth between the terms glass ionomer (GI) and glass ionomer cement (GIC). For all practical purposes, we will be referring to the same product. However, technically “glass ionomer” is a classification and “glass ionomer cement” is a glass ionomer used for cementing applications. Do not worry about this distinction. Quite often you will hear the term glass ionomer cement when one is referring to a restorative filling material application.

Our goal is to understand what glass ionomers are, how they are categorized, what are the reactions involved that will affect clinical manipulation and performance, how the release and recharge with fluoride ions, and what are the current applications.
The first dental product appeared as Dentsply ASPA. [CLICK] Quickly, other companies developed similar products. [CLICK] Over their more than 30-year history, glass ionomers have never been quite as good as bonded composites for any application. Looking back, it almost seems as though glass ionomers have been reborn many times – and so the comment about “the many faces of glass ionomers.”

In the competition between glass ionomers and composites, glass ionomers have lagged behind by 3-5 years in terms of their development. Small filler sizes, better matrix designs, and a host of other changes occurred first in composites and later in glass ionomers. Even if glass ionomers were competitive with composites in potential properties, they were never improved fast enough and lost many of the marketing battles. Today, the two major applications for glass ionomers are as resin-modified glass ionomer cements for luting fixed appliances and as ART restorations. We will be carefully explained shortly.
**TERMINOLOGY**

Don't be confused by some of the strange language.

**Glass Ionomer:** “glass” refers to the glassy ceramic particles and the glassy matrix (non-crystalline) of the set material, while “ionomer” refers to ion-crosslinked polymer.

**Polyalkenoic or Polyalkenoate:** refers to polymer chain which incorporates alkenoic monomers such as acrylic acid, tartaric acid, maleic acid, etc.

**F-Release:** refers to release of fluoride ions but there is no implication as to the source of the ions -- and there are many possibilities. The confusion for current systems is, if “F” does not come from the traditional GI matrix, then some people say that the system is not a “true” GI (but the point is irrelevant).

**Multiple-Cure:** refers to multiple curing mechanisms possible with resin-modified systems -- the terminology was first introduced in 1992 by 3M for their Vitremer product because it underwent the (1) traditional GI chemical setting reactions, (2) a self-cured polymerization reaction, and (3) light-cured polymerization reaction.

The original term "glass ionomer" was derived from the descriptors for the filler and the matrix components. [CLICK] The filler is a silicate “glass.” The matrix is ion-crosslinked (“ionomer”). [CLICK] The technical term in chemistry for these materials is polyalkenoic or polyalkenoate cement. While Europeans are adamant that only the technically correct term should be used, most of the rest of the world uses the terms glass ionomers, or GIs, or GICs.

[CLICK] All glass ionomers are capable of fluoride ion release. However, materials other than glass ionomers may release fluoride ions as well. There is nothing magical about if or how fluoride ion is released.

[CLICK] Glass ionomer setting reactions are complex and involve many options or stages. For that reason, some products have been designated as having multiple cures. These refer mainly to separate reactions and not multiple methods of inducing the setting reaction.
Glass ionomers are a “hybrid” formed from two earlier dental cement products, [CLICK] “silicate cement” (which contributes the powder portion) and [CLICK] “polycarboxylate cement” (which contributes the liquid portion). [CLICK] The hybrid was created to combine the best properties of the two materials. However, such marriages are never really truly perfect.

Silicate cement is formed when silicate glass powder particles react with phosphoric acid solution. A composite structure results that is a complex matrix of reaction products surrounding mostly unreacted silicate glass filler particles. The cement is soluble and tends to release F ions that are part of the matrix. Hence, the reputation for silicate cements as caries preventing restorations. Yet, continued dissolution always led to rough surfaces that absorbed stain and discolored. Therefore, the esthetics were limited to just a very few years at best.

Polycarboxylate cement forms from the reaction of ZnO powder particles with a polyacrylic acid solution. Zinc ions are released that chelate carboxyls on the polymer chains and produce crosslinking. The final material is a polyacrylate gel surrounding the reinforcing ZnO filler particles. This cement’s claim-to-fame is that the liquid solution (while initially acidic) is based on large molecules with little tendency to migrate into dentin or down dentinal tubules. It is viewed as more biocompatible (less irritating to the pulp) for this reason. The material is strong. The same carboxyls that undergo crosslinking are also capable of chelating available Ca ions on the surface of enamel or dentin causing chemical bonding and good adhesion. Since the cement is based on water, it wets tooth structure well.
Glass ionomers exist as an aqueous solution. [CLICK] The set product is a hydrogel. [CLICK] It is hydrophilic. It requires a certain amount of water to be stable. Removing the water, destabilizes the chelation. While this is an advantage in terms of wetting and chelating tooth structure, it is a disadvantage for strength and esthetics. The hydrogel can not be made to be as strong as a typical hydrophobic composite system. The water also refracts light making the colors of glass ionomers more opaque in appearance. They never achieve the excellent translucency of composites or ceramics.
Imagine tooth structure as an adherend portrayed to the left in the slide above. A single alumino-silicate particle is shown at the top surrounded by a milieu of ions released from the edges of the particle. [CLICK] A couple of polyacrylic acid polymer chains are revealed [CLICK] as partly ionized in the watery matrix. [CLICK] Calcium ions which have been released from the particles form [CLICK] divalent crosslinks between chains at first. [CLICK] These are replaced gradually over 1-3 days [CLICK] by trivalent crosslinks from aluminum ions. [CLICK] Fluoride ions in the matrix tend to quickly diffuse outward into aqueous surroundings. At the same time, the pendant carboxyls that are reacting with ions, may also react with partially ionized calcium ions on the surfaces of the powder particles and on tooth structure to create chemical bonds. [CLICK] Long after these processes have been completed, the siliceous network develops within the hydrogel.

To improve the properties of the final hydrogel and to increase the setting speed of the cement, a number of modifications have been explored over the last 30 years. To understand these effects (and the subsequent applications for modified GI cements) consider the following map of glass ionomers.
Glass ionomers have evolved in most cases to become more and more like composites. Starting at the middle of the bottom of this map, we can trace the evolution of the materials from a traditional hydrogel toward the upper right-hand corner that represents a standard hydrophobic composite.

The first substantial modifications to glass ionomers were made by adding presumed reinforcing fillers. Amalgam alloy powder was admixed with conventional GI to produce metal-modified GIs (MM-GI or MM-GIC). However, since the Ag-Sn alloy particles were not well-bonded to the matrix, the admixture was actually weaker. This was proposed at a time that dental amalgam was first coming under fire in the U.S. (about 1982) due to its Hg content. The admixture was called the "miracle mixture" and substituted for dental amalgam in some practices. Unfortunately its poor properties were quickly revealed and all such restorations had to be replaced. Yet, this mixture is still sold today as an alternative for build-ups or cores. Another version of MM-GIs was developed by adding metallic particles with ceramic coatings (cermets) as reinforcing fillers. These have continued to be used as cores.

A major hurdle for GI acceptance was overcome when water-soluble acrylic monomers (predominantly HEMA) were added along with double-bond functional polyacrylic-acid chains and initiators. These were called resin-modified glass ionomers (RMGI). It was now possible to visible light cure (VLC) the materials to achieve high early strength and more protection of the hydrogel. The same GI reactions still took place, but they were secondary for the performance of the materials.

Compomers eliminated the need for GI chemistry altogether. They were simply composites with the inclusion of fluoride releasing alumino-silicate glass filler particles. Another way of thinking of these materials is as GI powder particles substituted into composites. They are truly composites.

In response to the criticism that compomers were not really glass-ionomer-like at all, pre-cured glass ionomer particles were blended into compomers to create giomers. However, these products are not really competitive with standard composites as filling materials or cements.

Finally, in the early 1990s, a version of traditional glass ionomer was targeted at a market called A.R.T. (atraumatic restorative technique). In second and third world regions in which dentistry is not readily available, it is important to halt caries before it completely destroys a tooth and leads only to extraction. ART materials were designed to be placed by non-dental personnel as a holding procedure to stop caries until the individual could be treated in a dental office. To increase the longevity, these products may have a small amount of polymer added for improved toughness and so they are called resin-reinforced glass ionomers (RR-GIs). The market for these materials is incredible expansive. This is the largest volume of GI sold today.

A more recent push toward universal cements has evolved a new class situated between RMGI and COMPOMER.
Now let's examine the mechanism and effectiveness of fluoride release from GI. During reaction about 10-15% of the alumino-silicate powder particle is dissolved, releasing the ions necessary for setting into the matrix. At the same time, fluoride is released as well and persists in the hydrogel. Once the material is placed intraorally, there is a strong osmotic pressure for fluoride to leave the cement. The environment outside of the cement has low or no fluoride concentration and so the driving force is the outward diffusion of fluoride. All the matrix fluoride ions are released from the cement in about 24 hours (at about ~20 ppm levels). After that time, the only remaining fluoride is within the powder particles. Release of fluoride from the powder particles occurs very slowly and produces very low concentrations (at about ~1-2 ppm).
In the figure above, the green line represents the original matrix contribution. [CLICK] The yellow line represents the slow long-term glass particle contribution. [CLICK] The red line represents the overall fluoride release from the cement. [CLICK]

The process of simply releasing fluoride ions is not cariostatic. Fluoride ion concentrations must be high enough to either increase the fluoride content of local enamel/dentin or cause biochemical death to nearby bacterial cells. [CLICK] An estimate of the current levels necessary to have a clinically important effect are about 10-15 ppm. Since the long term average concentration is much lower, there is little if any biological advantage for these materials.

Over the last few years there have been efforts to “recharge” the material (i.e., add fluoride back into the restorations for subsequent release) by exposing the surfaces to fluoride ion sources. [CLICK] Quite a few things can push fluoride back into cements or restorations. This is simply a way of changing the osmotic pressure. If the concentrations on the outside are higher than the inside, then fluoride ion moves in rather than out. The best way to make this happen is with fluoride containing toothpastes, fluoride mouth rinses, or topical fluorides. This temporarily boosts the fluoride concentration. [CLICK] However, quickly this falls back to original levels again. [CLICK] Unfortunately, the boosted levels are not high enough for even a short time to be considered clinically efficacious as an anti-caries therapy.
It would have wonderful to have had well-designed, long-term clinical trials that tested the efficacy of fluoride release on caries reduction. However, any trial would have been very expensive to conduct. All manufacturers side-stepped this option. The problem for a clinical trial would be to exclude the fluoride that is present in the rest of the environment (food, beverages, drinking water, etc.) so that only the restorative material effect could be observed. Instead, for 25-30 years everyone has relied on circumstantial or anecdotal evidence to argue that these materials must be providing some anti-caries effect. In fact, there was no real effect at all. [CLICK] In the middle 1990s, this suspicion began to surface as more and more surveys of practitioners revealed that glass ionomer restorations were actually failing at a faster rate than amalgams or composites and because of secondary caries.
APPLICATIONS
GI have been tried for about every conceivable application.

1. Cement
2. Liner / Base
3. Restoration
4. Core / Foundation
5. (Tunnel Restoration)
6. (Sandwich Restoration)
7. Retrograde Filling Material
8. P/F Sealant
9. Root Caries Cervical Restoration
10. Temporary, or ART Restoration

Technical modifications:
- P/L \rightarrow Precapsulated
- Addition of etching and then BA
- Addition of different reinforcing fillers
- Finer and finer particle sizes

General Properties:
- Strength
- Adhesion
- Biocompatibility
- Fluoride release

Now let's examine the plethora of glass ionomer applications. These individual situations will be discussed in more detail by Dr. Wilder. Here is a capsular summary. [CLICK] Cements are popular applications for GI – to attach crowns and bridges to tooth structure. [CLICK] GI liners and bases are used by half the folks in practice but are not used by the other half. [CLICK] Glass ionomer restorations are losing more and more to composites. [CLICK] Cores or foundations for fixed prosthetics are popular but not as durable as composite or amalgam. [CLICK] Tunnel restorations are MO or DO restorations formed under marginal ridges without breaking them. [CLICK] Sandwich restorations are composites bonded over GI with the GI exposed as surfaces in some cases for fluoride release. [CLICK] Retrograde filling materials are root canal fillings of teeth that are removed, filled, and replanted. [CLICK] Sealant applications have not fared well because GI tend to be brittle. [CLICK] Cervical restorations are hard to restore because of moisture control challenges – so traditional glass ionomers are often preferred because of the ability to work in wet fields. [CLICK] Temporary restorations in permanent teeth or ART restorations in primary teeth are extremely popular.

In all cases, the sophistication of the restorative product has improved. [CLICK] Originally all glass ionomers were made by mixing powders and liquids but now most are pre-capsulated. Most have bonding agent options. Reinforcing fillers and much more careful powder phase grinding have improved handling, wear resistance, and esthetics. [CLICK] In general, the major reason for selecting a glass ionomer instead of a composite is because of challenges for moisture control, since they tend to demonstrate some adhesion to tooth structure in the presence of moisture.
In your handout, we have tried to include a comprehensive list of all products (old and new) for future reference. What will be confusing is that there is not logical correlation among types of glass ionomers (GI, RMGI, MM-GI, …) and various applications (filling material, core, cement, …).
Here are just a few examples are shown of the types of materials from the previous list. Note the different delivery systems that are involved.

Hytac and F2000 are compomers. Dyract Flow is a flowable version of a resin-modified glass ionomer. Fuji I LC is a light-cured RMGI that has substantial quantities of glass ionomer components in the overall cement. Vitremer is a common RMGI that is extremely popular as a lining cement over calcium hydroxide for deep amalgam or composite restorations.
A.R.T. RESTORATIONS
ART = Atraumatic Restorative Technique

Developed as temporary restorations for 3rd world countries. First tested in African countries. Now used widely in Asian countries.

Original technique = scoop, finger mix, finger insertion. Current technique = P/L or precapsulated mixture.

Now being used as permanent restoration in pedodontics.

ART is an acronym for “Atraumatic Restorative Technique.” [CLICK] This procedure was designed to combat rampant caries in second and third world regions around the globe where immediate dental care was not available. Patients with rampant caries were treated by non-dental personnel or themselves by scooping out caries, mixing P/L components between their thumb and forefinger into a ball, and plugging the hole to create a temporary restoration. [CLICK] These materials (of which Fuji IX has been the most widely used) release some fluoride but succeed mostly because they are capable of producing a good seal to tooth structure, are sufficiently tough to resist fracture, and can be easily repaired. They are simply a holding procedure to buy time (perhaps 12-18 months) until a patient can get to a normal dental clinic and receive professional care. [CLICK] The remarkable offshoot is that these materials perform better than expected and often provide 3-4 years of service. For that reason, pediatric dentists now consider ART materials as substitutes for both amalgam and composites. They can be easily placed and do not require special isolation techniques.
In the absence of widespread dental care, W.H.O. is using ART throughout the world as a first line defense to prevent dental caries from causing loss of the entire tooth. ART is being delivered by para-dental people who are minimally trained. It can be performed in many public settings such as local schools without any special furniture to seat the patient. It only requires the simplest of tools, such as a mouth mirror, explorer, head lamp, mixing pad, and matrix strip, and can be accomplished in an extremely short time.
Due to the ART application, Fuji IX has become a major success story for glass ionomers. [CLICK] Since the material has so many special applications for both clinical and laboratory use, the term “general purpose” has been appended (i.e., GP). Currently, an even faster setting version is available (Fuji IX GP FAST). While other products that are similar are arriving on the landscape, Fuji IX is clearly the leader.

One of the advantages of the initial stickiness of Fuji IX is that it works well as a temporary restoration in which some adhesion to tooth structure is required. Most of the faculty in the department use and promote this product. At the moment, I have Fuji IX in my own mouth replacing a sheared off facial cusp on tooth #16. It shows remarkably good short-term performance, except in the presence of red wine for some strange reason. This is an ongoing experiment, ☺.

This material should be part of any regular dental practice.
Please study all of the multi-choice questions and answers in preparation for any dental materials questions on your course exams.

THANK YOU.